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SOLUTION RATE AND POTENTIAL OF DISSOLVING CHROMIUM

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Notwithstanding the large number of research papers on the reaction of metals with solutions, little research has been done on the kinetics of the reactions between metals and concentrated solutions of acids. Moreover, almost all published research on the reactions of metals with acids are marked by the absence of a parallel determination of the potential of the metal in solution. And when the potential of the metal being dissolved is unknown, any effort to handle the observed behavior patterns of the metal's rate of solution becomes too arbitrary a matter.

The present paper is one of a series of research projects carried out in our laboratory on the parallel investigation of the rates of solution and the potentials of dissolving metals.*

EXPERIMENTAL METHOD

In the present research we employed, in the main, the same experimental method as in the earlier paper by the present authors on the rate of solution of magnesium [2], and we shall therefore take up in detail at this point only those factors in which our present method differs from those described in the paper mentioned.

Preparation of Sheets of Electrolytic Chromium

In the present research we investigated the rate of solution of sheets of electrolytic chromium, which were prepared in the following manner.

The electrolyte consisted of a 25% solution of chromic anhydride, slightly acidulated with sulfuric acid. Electrolysis was effected with a current density of 60 amp per sq. dm. of cathode surface, at a temperature of 25° ± 1°. We used a cathode of type metal. A cathode of this metal is convenient, for it does not deform even when a thick layer of chromium is deposited on it, and, besides, it dissolves easily in nitric acid. The back of the cathode was covered with bakelite lacquer; its front surface was divided into several parts by thin transverse strips of bakelite lacquer. The cathode was then subjected to heat treatment to polymerize the bakelite.

After electrolysis was complete, the cathode, together with the chromium deposited thereon, was cleaned of its bakelite and then subjected to the action of dilute nitric acid, the base of the cathode dissolving, and the chromium falling apart into separate sheets (according to the bakelite divisions). The edges of the chromium sheets thus obtained, 0.5 to 0.7 mm thick, were ground down on a carborundum wheel until the sheets were rectangles 1.5 x 3 cm in size. The sheets were again carefully washed in nitric acid and then in distilled water, after which they were placed in a special holder in the instrument for dissolving metals. The instrument as well as the metal holder are described in the above-mentioned paper by the present authors [2], (p. 237, Fig. 1).

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* It should be stated that this research was completed before World War II. Some of the experimental results having been published in Y. V. Durdin's article 'Electrochemical Mechanism of the Solution of Metals in Acids' [1].

In the present investigation the metal holder was modified so as not to end in a glass scoop for attaching a magnesium cylinder, but in a flattened glass bell, open at the bottom, within which a chromium sheet was attached with dental cement. To make the contact necessary for measuring the potential of the dissolving chromium, mercury was poured into the bell of the holder; this provided a fully dependable contact with the chromium sheet protruding beyond the edge of the cement.

On the outside, the cement, the rear surface of the sheet, and its edge were covered with bakelite lacquer, after which the whole was subjected to heat treatment to polymerize the bakelite. This operation was repeated 2-3 times. It should be mentioned that the shining side of the sheet, which faced the cathode during electrolysis, was covered with bakelite, while dissolution took place on the outer, grayish-velvety surface of the sheet.

Moreover, the chromium deposited in a freshly prepared bath may contain some impurities, and we therefore did not use the chromium obtained in the first 3 or 4 electrolyses. The chromium deposited thereafter was extremely pure. Spectral tests disclosed the presence of absolutely no impurities.

We used chemically pure hydrochloric and sulfuric acid of domestic origin in our experimental research on the solution rate of chromium. Dissolution was effected in apparatus of the type described in the above-mentioned paper by the present authors. In the present research, the volume of the apparatus was increased to 1.5 liters, and as a result the acid concentration did not vary by more than 1 or 2% even in the most prolonged tests.

Before starting a test, the solution in the apparatus was always saturated with hydrogen. The rate of solution of the metal was measured by the amount of hydrogen liberated, using a gas burette. The rate of solution of the chromium, v, was always expressed in terms of cubic centimeters of hydrogen* liberated per minute per square centimeter of chromium surface.

The potential of the dissolving chromium was measured by a compensation method with respect to a saturated calomel electrode. Henceforth, we shall call this potential, but with a plus sign, the potential of dissolving chromium.

The tests were made in a thermostat at a temperature of $40° \pm 0.1°$. It should also be stated that owing to the high test temperature and the rather high acid concentrations in which the chromium was dissolved, we used an electrolytic switch consisting of three glass tubes fused together to form an H. Gooch-crucible asbestos, soaked with a saturated solution of potassium chloride, was packed into the horizontal crossbar of the H. The sides of the H were filled as follows: into one there was pumped the solution in the apparatus, and into the other a saturated solution of potassium chloride; then the tops of the tubes were closed.

EXPERIMENTAL DATA

Hydrochloric Acid

1. Rate of Chromium Solution as a Function of Solution Time.

Sheets of chromium become covered with a permanant oxide film when allowed to lie about in the air. When such a sheet is place in an acid solution, it may not dissolve for a fairly long time. This initial passivity may be manifested most readily in sulfuric acid, but it may also occur in more highly diluted solutions of hydrochloric acid. For this reason, we always activated the chromium to shorten the length of the test runs. In the experiments on the solution of

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*The hydrogen volume was, of course, reduced to standard conditions.

chromium in hydrochloric acid this was done by plunging the chromium sheets into a solution of 10 N hydrochloric acid for 1 minute before they were placed in the test apparatus (the method of activating the chromium in the sulfuric-acid tests will be described under the appropriate heading).

This method of activating the chromium usually eliminates or greatly shortens the time during which the chromium is entirely passive, but it does not do away with the initial change in the rate of solution of the chromium with time (in hydrochloric acid). Typical curves representing the variation of the rate of solution of chromium with the time of its dissolution in 0.5 N, 1.5 N, and 4 N hydrochloric acid are given in Fig. 1. In this figure the chromium solution time is plotted on the abscissas axis in hours, the ordinates being the solution rate for Curves 1, 2, and 3, and the potential of the dissolving chromium for Curves 1' and 2'.

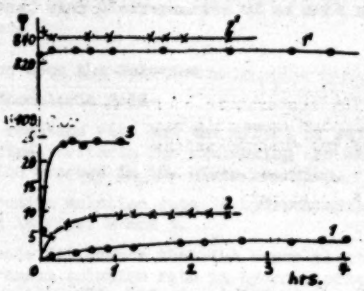

Fig. 1

As is seen in the figure, the rate of solution of chromium in dilute hydrochloric acid involves a rather long induction period,* during which the rate of chromium solution rises gradually.

After the end of the induction period the rate of chromium solution took on a constant value in our tests, remaining constant until all the chromium sheet was used up.

It is seen at once from Fig. 1 that as the acid concentration is raised, the chromium solution rate rises and the induction period rapidly decreases. It is hard to discern the induction period in 9-10 N concentrated solutions of hydrochloric acid, it lasting usually less than one minute at these concentrations.

As Fig. 1 indicates, the potential of the chromium dissolving in hydrochloric acid grows constant somewhat earlier than the chromium solution rate, the potential of the dissolving chromium varying only very little, as a rule, during the test, less than 5 millivolts. In some tests, however, we observed variations of the potential of as much as 10 millivolts. It should also be stated that – contrary to the behavior of the potential of dissolving iron, which will be described in one of our subsequent reports – the changes in the potential of dissolving chromium follow no fixed trend with time, i.e., we found instances where the potential of the dissolving chromium rose a few millivolts toward the end of the run, as well as cases where it fell.

Several tests were made at each acid concentration. Owing to the large amount of data, we shall not reproduce the overall table covering all the tests, but merely state that the following conclusions may be drawn from a comparison of the results of repeated experiments.

Fluctuations in the value of the chromium solution rate are fairly large, the mean arithmetical experimental error $\Delta v\%$, expressed in per cent, is greatest at fairly low acid concentrations. For example $\Delta v\%$ was about 12% for 1 N hydrochloric acid, and about 3-5% for 10 N acid.

These variations in the chromium solution rate are due, apparently, to the fact that the chromium sheets are not all completely identical, despite our

*The term 'induction period' is defined as the time elapsing from the instant the chromium is plunged in the solution until its solution rate becomes constant.

maintenance of standard conditions during the deposition of the chromium sheets.

With this in mind, we always endeavored, when determining the effect of any one factor, such as temperature, intensity of stirring, etc., on the chromium solution rate, to make tests, whenever possible, in which the solution rate of a single chromium sheet was observed at various values of this factor.

As for the potential of dissolving chromium, it should be pointed out that although the average deviation of potentials corresponding to the various tests run in acid at a given concentration from their mean value was of the order of 5 millivolts, the discrepancy between the potentials found in two parallel experiments was about 10 millivolts sometimes, with discrepancies of as much as 17 millivolts observed in individual cases.

Effect of Stirring the Solution Upon the Solution Rate of Chromium in Hydrochloric Acid

The temperature coefficient of the reaction rate and the effect of stirring the solution upon this rate are the principal criteria for evaluating the magnitude of the kinetic weight of the diffusion process in the given reaction.

The effect of stirring upon the chromium solution rate in hydrochloric acid is illustrated by the curves plotted in Figs. 2 and 3.

Figure 2 is like Fig. 1, with the sole difference that the curve plotted in Fig. 2 expresses the variation of the chromium solution rate in hydrochloric acid (1 N) with time for different stirring rates: 370, 630, 0 and 370 rpm of the stirrer. Figure 2 shows at once that the solution rate of chromium in 1 N hydrochloric acid is completely independent of the stirring rate.

Nor does a change in the stirring rate from 370 to 630 stirrer rpm have any effect upon the potential of the dissolving chromium, as is also seen in Fig. 2. When the stirrer was stopped completely, the potential was observed to rise slightly, by 9 millivolts, in this test run.

Fig. 3 illustrates the effect of stirring upon the rate of chromium dissolution in solutions of hydrochloric acid of varying concentrations. The ordinates in this graph represent the chromium solution rate, while the rpm of the stirrer, v, are plotted as abscissas.

Fig. 2.

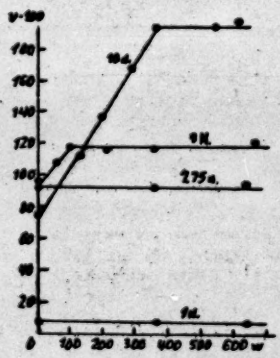

Fig. 3.

We see from Fig. 3 that the chromium solution rate is unaffected by the intensity of stirring; this is so not only for 1 N hydrochloric acid, but for hydrochloric acid that is about 8 N (7.75 N). On the other hand, stirring exerts a quite special effect upon the chromium solution rate at higher concentrations of hydrochloric acid. This peculiarity consists of the following: when the stirrer is started, the chromium solution rate first rises rapidly with increasing stirrer rpm. But when the rotational speed of stirrer reaches a certain rpm, the chromium solution rate becomes independent of the rate at which the solution is stirred.

In 9 N hydrochloric acid, this critical speed of the stirrer was about 100 rpm in our apparatus, as is seen in Fig. 3.

As is seen in Fig. 3, this critical speed rises quickly as the acid concentration is increased. At 10 N HCl it is about 300-400 rpm.

Thus, we can say that when chromium is dissolved in hydrochloric acid, the solution rate is a function of the rate at which the solution is stirred only at high acid concentrations and is of the specific nature described above.

The effect of stirring upon the potential of dissolving chromium was not investigated by us in all our experiments. Nevertheless, it may be said that at hydrochloric-acid concentrations below 10 N the potential of dissolving chromium was practically independent of the rate at which the solution was stirred. (In 1 N hydrochloric acid, the potential rose slightly, by a few millivolts,* in some cases when the stirrer was stopped).

In 10 N hydrochloric acid, on the other hand, we observed a marked rise in the potential of dissolving chromium when the rate at which the solution was stirred was raised; this rise was as much as ~20 millivolts when the stirrer speed was raised from zero to 550 rpm. As will be shown in one of our subsequent papers, however, this change in the potential is not the cause of the variation of the chromium solution rate with the rate of stirring observed in 10 N HCl.

3. Temperature Coefficient of the Chromium Solution Rate in Hydrochloric Acid

To determine the temperature coefficient of the chromium solution rate we ran special experiments in which a given sheet of chromium was first dissolved at a certain temperature. When the chromium solution rate had grown constant at this temperature, the temperature was changed, and the constant solution rate of the same chromium sheet was determined at the new temperature, etc., etc.

Figure 4 serves as an illustration of one of these tests. In this figure time in hours is plotted as the abscissa, and the chromium solution rate as the ordinate. The curves shown in this graph express the chromium solution rate as a function of time for the temperatures marked on the curves. The test was made in 1 N HCl with $\underline{v}$ = 370 rpm.

Fig. 4

The results of some of these tests for 1 N and 10 N hydrochloric acid are listed in Table 1.

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* It should be remembered that we refer to a chromium potential as measured against a calomel electrode, but with a plus sign, so that an increase in potential signifies a transition to a poorer value.

TABLE 1

Temperature Coefficient of the Chromium Solution Rate in Hydrochloric Acid

Solution	NCr	t°C	W	v x 100	A	α%	$\frac{v_{t+10}}{v_t}$	φ
1 N HCl	9	20	370	1.08	14.400	8.7	2.4	797
	9	30	370	2.60	15.900	8.4	2.3	815
	9	40	370	6.03	17.000	8.5	2.3	852
	9	50	370	14.1				843
	10	30	370	3.4	14.800	7.8	2.2	807
	10	40	370	7.85	15.600	7.9	2.2	821
	10	50	370	16.00				833
4 N HCl + 0.5 N KCl	3	30	370	2.7	16.000	8.4	2.3	821
	3	40	370	6.3	17.300	8.5	2.4	839
	3	50	370	14.9				
10 N HCl	29	30	370	85,5	13.700	7.2	2.06	854
	29	40	370	176				846
	29	30	0	38.5	13 300	7.0	2.02	843
	29	40	0	78.0				827
	30	30	0	35.5	13.800	7.3	2.08	837
	30	40	0	74.0				828
	30	30	550	91.0	13.300	7.0	2.02	848
	30	40	550	183				846
	15	30	370	85	15.300	8.0	2.25	-
	15	40	370	191				-
	15	30	0	40.5	15.300	8.0	2.25	-
	15	40	0	91				

Mean values:

1 N HCl: $A = 16000 \pm 700$; $\alpha\% = 8.3\%$; $\frac{v_{t+10}}{v_t} = 2.3$

10 N HCl: $A = 14500 \pm 1000$; $\alpha\% = 7.4\%$; $\frac{v_{t+10}}{v_t} = 2.1$

In this table NCr denotes the number of sheets of chromium used in the given test; $\underline{v}$ = stirrer rpm; A = critical increment of the chromium solution rate, computed from the Arrhenius equation $\lg v = \frac{A}{RT} + B$; $\alpha\%$ = temperature coefficient of the chromium solution rate, expressed as per cent per degree; and φ = the potential of dissolving chromium. The significance of the other notation is self-evident.

The straight line in Fig. 5 represents the variation of lgv with $\frac{1}{T}$ in one of our tests. Figure 5 and Table 1 enable us to say that the temperature variation of the chromium solution rate is in good agreement with Arrhenius' equation, the magnitude of the temperature coefficient of the chromium solution rate in 1 N as well as in 10 N HCl corresponding to the normal value of the temperature coefficient for the velocity of chemical reactions.

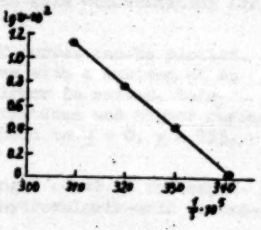

Fig. 5

4. Chromium Solution Rate as a Function of the Concentration of Hydrochloric Acid

The chromium solution rate was investigated by us in hydrochloric acid solutions whose concentrations ranged from 0.5 N to 10.5 N.

Figure 6 shows the curves that express the variation of the chromium solution rate with hydrochloric-acid concentration as found by us. In this figure the hydrochloric-acid concentration is plotted in normalities along the axis of abscissas, the mean value of the chromium solution rate being plotted along the axis of ordinates. The numbers above the points denote the number of determinations on which the mean value of the given rate is based. Where no number is given, the point in question was plotted on the basis of a single experiment.

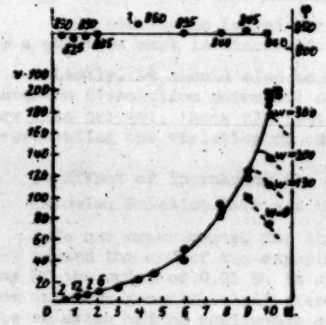

Fig. 6.

At the top of the axis of ordinates there are also plotted the potential values.

The straight line across the top of the figure represents the variation of this potential with the hydrochloric-acid concentration. The figures near the several points on this line denote the respective values of the potential for the points in question.

The solid curve in Fig. 6 expresses the variation of the chromium solution rate with the hydrochloric-acid concentration for values of $\underline{w}$ that exceed the critical value; i.e., this curve corresponds to chromium solution rates obtained at stirring speeds at which the chromium solution rate is no longer a function of increases in the stirrer speed.

The points on the dotted sections of the curve were obtained for values of

$\underline{v}$ below the critical value of this variable in hydrochloric acid at the given concentration.

The corresponding values of $\underline{v}$ are given in the graph.

According to Fig. 6, there is only one curve of v (c_{HCl}) in the range of hydrochloric-acid concentrations from 0.5 N to about 8 N that expresses the chromium solution rate as a function of the hydrochloric-acid concentration for all rates at which the solution is stirred.

At high HCl concentrations two different kinds of curves can be plotted. When the solution is not stirred ($\underline{v} = 0$), we get a curve with a maximum at an acid concentration of about 8 N. As the rpm of the stirrer is raised, this maximum shifts toward the region of higher acid concentrations and higher chromium solution rates of the curves in Fig. 6 that correspond to $\underline{v} = 0$, $\underline{v} = 133$, $\underline{v} = 200$, and $\underline{v} = 300$ rpm).

At values of v that exceed 300 rpm there is a single curve of the exponential type without a maximum for the entire range of hydrochloric-acid concentrations investigated by us.

This duality in the variation of the chromium solution rate with acid concentration evidently is a direct consequence of the peculiar effect of stirring upon the chromium solution rate described in section 2.

Still another fundamental fact follows from Fig. 6, namely, that the potential of chromium dissolving in hydrochloric acid may be taken as constant in the first approximation and equal to 0.85 ± 0.01 volt.

It should be noted, however, that a more detailed study of all the data on the potential of dissolving chromium leads to the conclusion that the potential of dissolving chromium has an evident tendency to rise slightly as the acid concentration is increased; it is probable that this rise is of the order of 10-15 millivolts and thus is canceled out by the experimental error.

This conclusion is reinforced by the data of Fig. 6 if the point denoted by a question mark is discarded.

Lastly, it should also be noted that unsytematic fluctuations of the chromium dissolution potential of the order of ± 0.01 volt from the mean value are also present; these fluctuations find no noticeable reflection in the curve representing the variation of chromium solution rate with acid concentration.

5. Effect of Increasing the Concentration of Cr^{++} Ions Upon the Chromium Solution Rate and the Potential of the Dissolving Chromium

In our experiments, the dissolution of the Chromium began in pure acid; but toward the end of the experiment the concentration of chromium ions usually was of the order of 0.01 N, in some experiments going as high as ~ 0.02 N when the chromium was completely dissolved. This accumulation of chromium ions in the solution had no noticeable effect upon the potential of the dissolving chromium or upon its solution rate. We could explain this fact by the circumstance that as soon as the metal begins to dissolve, a certain concentration of its ions is immediately formed at its surface, it being quite conceivable that this concentration attains a level of hundredths of normal at extremely low metal solution rates, such as the rate of dissolution of chromium in hydrochloric acid that is $\sim 1 - 2$ N.

This is why we set up a special experiment in which the concentration of chromium ions in the solution was artificially raised to a concentration of 1 N.

When chromium dissolves in hydrochloric acid, it enters solution as bivalent ions. Solutions of bivalent chromium oxidize very easily, which is why setting up experiments to determine the effect of the concentration of Cr^{++} ions upon its solution rate encounters several difficulties.

This experiment was set up by dissolving a weighed quantity of electrolytic chromium in 3 N hydrochloric acid so as to yield a solution of 2 N HCl + 1 N $CrCl_2$.

The values of the chromium solution rate and the potential of dissolving chromium were measured at $\underline{v}$ = 370 rpm, $\underline{v}$ = 0 rpm, and again at $\underline{v}$ = 370 rpm.

Table 2

	$\underline{v}$ = 370	$\underline{v}$ = 0	$\underline{v}$ = 370
v x 100	12.5	13.1	13.2
φ mV	827	833	824

The data in the table indicate that even when a high concentration of Cr^{++} ions is present, the chromium solution rate is unaffected by stirring the solution, as was the case in pure 2 N HCl.

According to Table 2, the mean value of the chromium solution rate, $\underline{v}$ x 100, is 12.9 ml/min, the potential ranging from 824 to 833 millivolts. When the chromium was dissolved in pure 2 N hydrochloric acid, the values of the chromium solution rate and of the potential φ were $\underline{v}$ x 100 = 11.5 ml/min and φ = 830-835 millivolts, respectively, according to the data in Fig. 6.

We may conclude from these data that increasing the concentration of Cr^{++} ions to one-normal exerts no appreciable effect (i.e, going beyond the limits of experimental error) on either the chromium solution rate or on its potential.

Sulfuric Acid

1. Induction Period

The laws governing the determination of the chromium solution rate in sulfuric acid differ fundamentally from the corresponding laws for dissolution in hydrochloric acid. This difference is chiefly manifested in the fact that the chromium's change from a passive to an active state takes place with much more difficulty in sulfuric acid than in hydrochloric acid. The rate of solution of electrolytic chromium immersed in a sulfuric-acid solution ordinarily remains zero for several hours; we therefore had to activate the chromium before using it in our sulfuric-acid experiments.

At first, we activated the chromium by immersing it in a solution of concentrated hydrochloric acid for one or two minutes. We later employed an electrochemical method of activating the chromium. This method consisted of immersing the chromium sheet, still in its holder, in a solution of sulfuric acid as one element of a couple with a sheet of platinum, the acid being of the same concentration as that used in the experiment proper. Current was passed through this circuit for a minute or two, the chromium sheet acting as the cathode. The metal holder was then quickly transferred to the reaction apparatus. Both methods yielded the same results, in respect of shortening the induction period as well as of establishing a constant chromium solution rate.

By way of example, curves representing the chromium solution rate and the potential of dissolving chromium as functions of time are shown in Fig. 7, Curves 1, 2 and 3 showing the chromium solution rate, and Curves 1', 2', and 3' the

potential. The beginnings of Curves 1, 2, and 3 are somewhat to the left of the origin, since the first reading of hydrogen volume usually is made a few minutes after the chromium has been immersed in the sulfuric acid. Curves 1 and 2 represent experiments with 1 N acid; Curve 3 is for an experiment with 3 N acid.

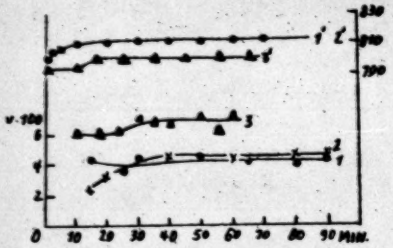

Fig. 7.

Curve 1 reflects the variation of the chromium solution rate with time for a chromium sheet that had been activated in concentrated hydrochloric acid. Curve 2 corresponds to another experiment with another sheet of chromium, which was activated with hydrochloric acid and then placed in a vessel containing 12 N sulfuric acid, where it was washed and allowed to dissolve for 5 minutes, after which it was placed in the reaction apparatus. As may be seen in Fig. 7, the chromium solution rate was the same in both cases, within the limits of experimental accuracy, after the steady state had been reached. Curve 2' expresses the potential of dissolving chromium as a function of time during the second test.

No corresponding curve was plotted for the first test, since it practically coincided with the one shown. This seems to indicate that the small quantity of chromium ions that enters the solution when the chromium is activated in hydrochloric acid evidently does not effect the experimental results. As we shall see later on, this fact is corroborated by the experiments on the effect of adding KCl upon the chromium solution rate in H_2SO_4.

Curves 3 and 3' indicate the chromium solution rate and the potential of dissolving chromium, respectively, in 3 N sulfuric acid, in these tests the chromium being activated electrolytically.

We see that curves of the same type are obtained with all the methods outlined above, the induction period being sufficiently brief in all instances - some 10 to 30 minutes.

2. Effect of Stirring Upon the Chromium Solution Rate in Sulfuric Acid and the Temperature Coefficient of this Solution Rate

In 1 N to 10 N sulfuric acid, the chromium solution rate positively does not rise as the stirring rate is increased. In fact, we observed the contrary phenomenon: the chromium solution rate rose slightly in fairly dilute solutions, from 1 N to 7 N, when the stirrer was stopped. The stirring rate has practically no effect upon the chromium solution rate in sulfuric acid whose concentration is 8 N to 10.5 N. Lastly, in 15 N sulfuric acid, the chromium solution rate rises sharply as the rate at which the solution is stirred is increased.

To illustrate this, we give in Table 3 the values of v/v^0, the ratio of the chromium solution rate at v = 600 rpm to the rate at v = 0 rpm for various concentrations of sulfuric acid.

The figures in Table 3 were obtained from data on the chromium solution rate derived by interpolation from the curves shown in Figs. 8 and 9.

As seen in Table 3, the drop in the chromium solution rate due to stirring

is extremely slight, actually lying within the limits of experimental error; we shall, therefore, confine ourselves to the statement that there is absolutely no increase in the chromium solution rate due to stirring in solutions of sulfuric acid at concentrations up to 10 N.

Table 3

$C_{H_2SO_4}$	2	4	6	8	10	15
v/v^0	0.85	0.90	0.90	1	1	2.8

In 15 N sulfuric acid we see that the chromium solution rate rises markedly as a result of stirring the solution, like the rise in the chromium solution rate due to stirring described above for 10 N hydrochloric acid.

The slight observed drop in the chromium solution rate due to stirring will be noted for the present as possibly of some interest, but we shall stipulate that this fact still requires checking, since its magnitude is so close to the experimental error.

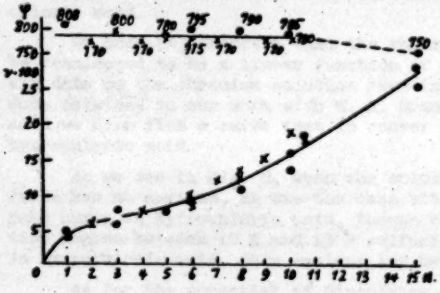

Fig. 8.

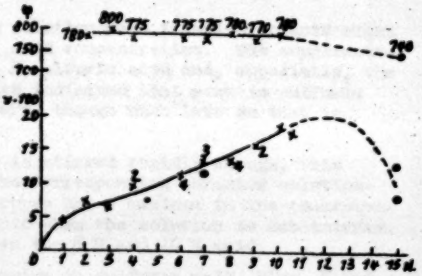

Fig. 9.

The very absence of any increase in the chromium solution rate in sulfuric acid as the result of stirring enables us to state that the kinetic weight of the diffusion process in this process is zero (with the exception of 15 N H_2SO_4).

This assertion is supported by the relatively low chromium solution rate in sulfuric aid; this is why the temperature coefficient of the chromium solution rate in sulfuric acid was determined only in two control experiments, one in 1 N sulfuric acid, and the other in 15 N sulfuric acid; in both tests v was 600 rpm.

These experiments yielded the following values for A, $\alpha\%$, and $\frac{v_{t+10}}{v_t}$.

Table 4

$C_{H_2SO_4}$	A	$\alpha\%$	$\frac{v_{t+10}}{v_t}$	
1 N	14.900	7.5	2.1	For the temperature range 40 - 50°
15 N	14.400	7.5	2.1	For the temperature range 30 - 40°

These figures show that the temperature coefficient of the chromium solution rate is high in sulfuric acid, both in 15 N acid and in 1 N acid.

3. The Chromium Solution Rate and the Potential of Dissolving Chromium as Functions of the Concentration of Sulfuric Acid.

The curves expressing these functions are shown in Figs. 8 and 9. The notation in these figures is the same as in Fig. 6. The data of Fig. 8 cover tests at $\underline{v}$ = 370 rpm; those in Fig. 9 are for tests in which there was no stirring.

The dots represent the initial test series, made by Y. Durdin with A.N. Markevich; the crosses represent a supplementary series of tests made by Y. Durdin and M.A. Oranskaya to clear up the problem of the effect of stirring on the chromium solution rate in sulfuric acid. As we see in Fig. 8, both test series yielded results that agreed fairly well with one another.

We see in Figs. 8 and 9 that the chromium solution rate increases much more slowly as the sulfuric-acid concentration is raised than was the case in hydrochloric acid.

We once [1] supposed that the chromium solution rate in sulfuric acid might be considered to be a linear function of the acid concentration. The supplementary data on the chromium solution rate in 15 N sulfuric acid and, especially, the data obtained in our work with M. A. Oranskaya indicated that even in sulfuric acid we also find a curve that is convex upward, though much less so than in hydrochloric acid.

As we see in Fig. 8, when the solution is stirred rapidly enough, this curve has no maximum, as was the case with the corresponding chromium solution-rate curve in hydrochloric acid, though the curve has a maximum in the concentration region between 10 N and 15 N sulfuric acid when the solution is not stirred. In hydrochloric acid, this maximum lay between the 8 N and 10 N acid.

As for the potential of dissolving chromium in sulfuric acid, Figs. 8 and 9 enable us to reach the following conclusions.

a) In the range from 1 N to 10 N sulfuric acid the change in the potential of dissolving chromium as the sulfuric-acid concentration is increased is very slight. The mean value of the potential of dissolving chromium in this concentration region may be taken as 0.78 ± 0.015 volt.

b) The indicated error of 15 millivolts is determined by the random fluctuations of the potential of dissolving chromium, which are somewhat higher in sulfuric acid than in hydrochloric acid. As is seen in Fig. 8, these fluctuations are as high as 20-30 millivolts in some instances, these potential fluctuations not affecting the curve of chromium solution rates appreciably, as was also true when chromium was dissolved in hydrochloric acid.

c) The potential of chromium dissolving in sulfuric acid is somewhat lower than the potential of chromium dissolving in hydrochloric acid: 0.78 volt as against 0.83 volt.

d) When the concentration of sulfuric acid is chnaged from 10 N to 15 N, an appredíable drop in the potential of dissolving chromium, of about 30 millivolts, is observed. In the sulfuric-acid concentration range from 1 N to 10 N we find that the potential remains constant, within the limits of experimental error. It may be thought, however, that even in this region of sulfuric-acid concentrations we have a slight drop of the potential, of the order of 5 to 10 millivolts, contrary to what occurs in hydrochloric acid.

Comparisons of the data in Figs. 6, 8, and 9 indicates that the differences

in the dissolution of chromium in hydrochloric and sulfuric acids are as follows: that the curve of $v(c)$ rises much more steeply in hydrochloric acid than in sulfuric acid, as a result of which the chromium solution rate in concentrated solutions of hydrochloric acid is many times as high as it is in sulfuric acid of the same normality.

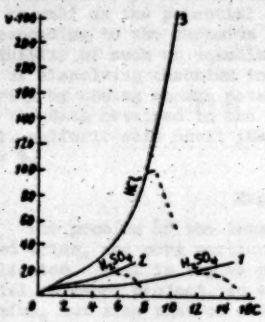

Fig. 10.

This difference may be mitigated somewhat if we assume that sulfuric acid dissociates in the first stage, on the whole, and compare the chromium solution rates in the two acids of equal molar concentration. To facilitate this comparison, Figs. 6 and 8 are plotted together in Fig. 10. In this figure, there are two curves for sulfuric acid; for Curve 1 the normality of the sulfuric acid is plotted along the axis of abscissas, with the molar concentration of the sulfuric acid being plotted there for Curve 2.

4. Effect of Adding KCl to Solutions of HCl and H_2SO_4 Upon the Chromium Solution Rate in These Acids

According to the foregoing, the chromium solution rate is greatly affected by the nature of the Cl' or SO_4'' anion. To ascertain the basic nature of this effect we ran several auxiliary experiments. In these experiments (which were of a preliminary nature), we first determined the solution rate of a given sheet of chromium in a solution of 1 N hydrochloric or sulfuric acid, after which enough potassium chloride was added to the acid solution to produce a solution of 1 N acid plus 0.5 N KCl; the solution rate of the same chromium sheet then being measured in the latter solution. These tests showed that in 1 N acids, whether hydrochloric or sulfuric, such an addition of potassium chloride and, hence, a corresponding increase in the concnetration of Cl' ions, exerts but a very slight influence upon the chromium solution rate, raising it by some 5 to 10%, so that this effect is close to the limits of experimental error.

The results are quite different when potassium chloride is added to concentrated solutions of sulfuric acid. The data for two such experiments are listed in Table 5.

Table 5

Composition of solution	v x 100	φ
7.5 mol. H_2SO_4	28	750
7.5 mol. H_2SO_4 + 0.1 mol. KCl.	41	768
7.0 mol. H_2SO_4 + 0.5 mol. KCl.	50	790
7.0 mol. HCl	65	833
5 mol H_2SO_4	16	790
5 mol H_2SO_4 + 1.8 mol. KCl ...	29	840
5 mol HCl	33	833

We may see by Table 5 that the addition of potassium chloride in decimolar concentration to 7-7.5 mol (14-15 N) sulfuric acid increases both the chromium solution rate and the potential of the dissolving chromium. Raising the concentration of the potassium chloride to 0.5 mole doubles the chromium solution rate and increases the potential by about 40 millivolts.

Moreover, as we see from the same table, it may be considered that as the concentration of potassium chloride is further increased, the chromium solution rate as well as the potential of the dissolving chromium would rise to values corresponding to the chromium solution rate in 7 mol... hydrochlori acid. The possibility of such an eqaulization of the chromium solution rate and the potential of dissolving chromium in hydrochloric and sulfuric acids of the same molarity by adding enough potassium chloride to the acid is likewise in agreement with the data obtained in the experiment in which potassium chloride was added to 5 mol. sulfuric acid until its own concentration reaches 1.8 normal, as seen in Table 5.

EVALUATION OF RESULTS

The problem of the laws governing the solution rates of metals in concentrated acids, and more particularly the underlying reasons therefor, are rather complicated. That is why we propose to make this problem the subject of a special research project, in which we shall examine not only the dissolution of chromium, but also that of other metals. In the present paper we shall confine ourselves, in the main, to a formal discussion of the foregoing experimental data.

1) In accordance with what has been stated above, the chromium solution rate is independent of the rate at which the solution is stirred in hydrochloric acid up to concentrations of 8 normal and in sulfuric acid in concentrations up to 10 normal, and we may therefore consider that in these concentration regions the chromium solution rate is unaffected by the process of diffusion, which likewise agrees with the high value of the temperature coefficient of the chromium solution rate.

In regions of higher acid concentrations – 9-10 N hydrochloric acid and 10-15 N sulfuric acid – the stirring rate exerts a marked effect upon the chromium solution rate, but with the specific peculiarities mentioned above.

It is significant, however, that the temperature coefficient of the chromium solution rate remains practically as high as in more dilute solutions. We shall endeavor to furnish an explanation of this phenomenon in one of our future papers.

2) This phenomenon of the effect of stirring upon the chromium solution rate is directly related to the general nature of the $v(c)$ curves, expressing the chromium solution rate as a function of the acid concentration.

According to our data, these curves have a maximum when no stirring takes place, but this maximum vanishes when the chromium solution rate is measured at a high enough stirring rate.

The maximum on the $v(c)$ curves in concentrated acid solutions was found long ago by Kayander during his research on the solution rate of magnesium [3].

In the case of chromium, curves exhibiting a maximum were recorded by E. Muller in his investigation of the solution rate of chromium in hydrochloric and sulfuric acids without stirring the solution [4].

This maximum was usually considered to correspond to the maximum on the curve of the acid's specific conductivity.

Our data indicate, however, that the reason for a maximum on the $v(c)$ curve (at any rate, in the case of chromium) cannot be a change in the acid's conductivity, inasmuch as this maximum vanishes when the rate at which the solution is stirred is increased.

When the rate at which the solution is stirred is high enough, the ...

variation of the chromium solution rate with the hydrochloric-acid concentration is expressed by an exponential curve of a type corresponding to those plotted by Tsentnershver for the solution rates of cadmium [5], tin [6], and aluminum [7]. At the time Tsentnershver held that explanation of these curves required abandoning the electrochemical mechanism of the solution of metals in acids and adopting a mechansim that he called a chemical one, according to which the solution of the metal takes place by its reacting with an acid molecule or with Cl' ions [8]. As Y. V. Durdin [1] and A.I. Shultin [9] demonstrated, however, this type of curve can also be brought into agreement with the electrochemical mechansim of metal dissolution by assuming that the factors governing the kinetics of this reaction are electrode processes. This possibility will be examined in detail in the special research referred to above.

3) According to our data, the potential of dissolving chromium in 1 N to 10 N hydrochloric and sulfuric acids is nearly constant: 0.83 ± 0.01 volt in hydrochloric acid and 0.78 ± 0.15 volt in sulfuric acid.

If we take the potential of the saturated calomel electrode with respect to the normal hydrogen electrode at 40° as 0.236 volt, we get the potential of dissolving chromium with respect to the normal hydrogen electrode, taken with a positive sign, as $\varphi = 0.59$ volt for hydrochloric acid, and $\varphi = 0.54$ volt for sulfuric acid. This value of the potential of dissolving chromium is close to the value of the normal potential of chromium usually cited: 0.56 volt.

Correspondingly, we previously [1] expressed the hypothesis that when chromium is dissolved, its potential is close to equilibrium. According to Latimer's data, however, the $Cr = Cr^{+++} + 3e^-$ reaction corresponds to a potential of 0.71 volt; whereas the $Cr^{++} = Cr^{+++} + e$ reaction corresponds to a potential of 0.41 volt. It follows that for the $Cr = Cr^{++} + 2e$ reaction we get $\varphi^\circ = 0.86$ volt as the equilibrium potential, taken (as we have done) with a plus sign, i.e., a value that is higher than what we have found as the potential of dissolving chromium. Bearing this in mind, we now believe it possible to assume that the anodic process of supplying metal ions to the solution is accompanied by an essential anodic polarization in the dissolution of chromium, of the order of ~0.25 to 0.30 volt.

SUMMARY

1. The chromium solution rate and the potential of dissolving chromium has been measured in hydrochloric and sulfuric acids.

2. It has been found that the chromium solution rate in hydrochloric acid at concentrations up to 8 normal and in sulfuric acid at concentrations up to 10 normal is independent of the rate at which the solution is stirred. This provides a basis for the conclusion that the chromium solution rate in these acids is unaffected by the diffusion process, at these concentrations, which agrees with the high temperature coefficient of this rate.

In solutions of higher concentrations, stirring has a marked effect upon the chromium solution rate.

3. The variations of the chromium solution rate with the acid concentration when the solution is not stirred is expressed by a curve exhibiting a maximum, the curve having no maximum when the stirring is vigorous enough.

4. The potential of dissolving chromium varies but little with concentration in the range from 1 N to 10 N hydrochloric and sulfuric acids; it may be taken as -0.59 ± 0.01 volt in hydrochloric acid and -0.54 ± 0.015 volt in sulfuric acid (with respect to the normal hydrogen electrode).

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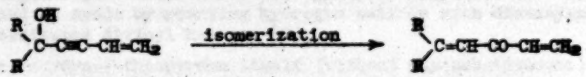
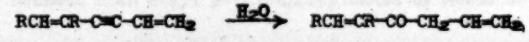
DERIVATIVES OF ACETYLENE

104. RESEARCH ON HETEROCYCLIC COMPOUNDS. X. A NEW METHOD OF SYNTHESIZING TETRAHYDRO-γ-THIOPYRONES BY THE ACTION OF HYDROGEN SULFIDE UPON VINYL ALLYL KETONE

I. N. Nazarov, A. I. Kuznetsova and I. A. Gurvich

Systematic research has been carried on for many years in our laboratories on various transformations of divinyl ketones and vinyl allyl ketones, which are readily synthesized by isomerizing vinylacetylenic alcohols [1] and hydrating divinylacetylenic hycrocarbons [2]:





R = hydrogen or alkyl

The extremely high reactivity of these ketones and their availability opened up new and extensive perspectives for organic synthesis on the basis of acetylene, including polycyclic and heterocyclic compounds.

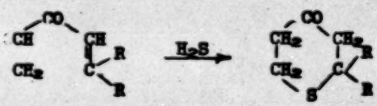
When divinyl ketones are hydrated in the presence of a mercury salt, tetrahydropyrones are formed, as has been shown earlier [3]:

It is only in exceptional cases that vinyl allyl ketones can be hydrated to tetrahydro-γ-pyrones (vinyl allyl ketone itself can be hydrated with extraordinary ease), as substituted vinyl allyl ketones are cyclized extremely readily by acids to cyclopentenones:

The action of ammonia and primary amines upon such vinyl allyl ketones gives rise to various γ-piperidones very easily [4]:

This reaction takes place much more smoothly with the divinyl ketones, owing to their instability and their ability to condense, forming γ-piperidones [5]:

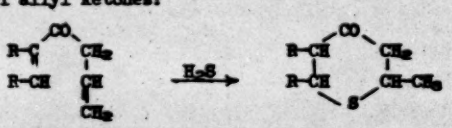
The action of hydrogen sulfide upon these divinyl ketones readily results in the formation of the formerly almost inaccessible tetrahydro-γ-thiopyrones, as shown in one of our previous reports [6]:



Single representatives of this group of compounds had been previously synthesized by Arndt by reacting hydrogen sulfide with dibenzylacetone and some other substituted divinyl ketones [7].

Tetrahydro-γ-thiopyrone itself (without any substituents) had been synthesized by Bennett from ethyl β-thiodipropionate by means of a Dockman condensation [8].

In the present paper we show that the most varied tetrahydro-γ-thiopyrones can also be easily synthesized, with yields of about 70%, by reacting hydrogen sulfide with vinyl allyl ketones:



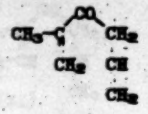
As with the divinyl ketones, the reaction is effected in an alcohol solution in the presence of sodium acetate, at 0° or at room temperature with subsequent boiling of the reaction mixture in order to cyclize the mercaptoketones that form at first. Thus, from vinyl allyl ketone itself we synthesized 2-methyltetrahydro-1-thiopyran-4-one (II), with a yield of some 30%, which was oxidized to a sulfone (III) by potassium permanganate:

(I) (II) (III)

As in reactions with ammonia and methylamine, the reaction of substituted vinyl allyl ketones with hydrogen sulfide is much smoother than is the case with vinyl allyl ketone itself, resulting in the formation of the corresponding tetrahydro-γ-thiopyrones with a yield of as much as 70%.

The action of hydrogen sulfide on allyl isopropenyl ketone (IV) yielded 2,5-dimethyltetrahydro-1-thiopyran-4-one (V), with a yield of 68%. This thiopyrone

was isolated in two isomeric forms (liquid and crystalline), which were oxidized by permanganate to the corresponding sulfones (VI). The two isomeric thiopyrones (V) form different 2,4-dinitrophenylhydroazones, but yield the same semicarbazone.



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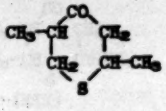
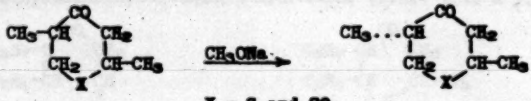


(V)

(VI)

When the liquid cis isomer of the thiopyrone (V) is boiled in a dilute solution of sodium methylate, it is converted into the solid trans isomer.

The sulfone of the cis isomer is converted into the trans sulfone under these conditions.



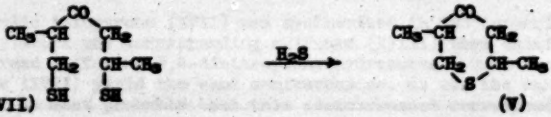
Cis form

X = S and SO_2

Trans form

We were the first to observe cis-trans conversions in the tetrahydro-γ-thiopyrones, but analogous conversions have also been described recently for the acids of the tetrahydro-γ-thiopyran series [9].

The action of hydrogen sulfide on allyl isopropenyl ketone in an acetone solution in the cold also resulted in the formation of a dithiol (VII), which is cyclized to the thiopyrone (V) by heating in an alcohol solution in the presence of sodium acetate:

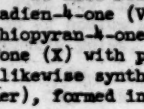


(VII)

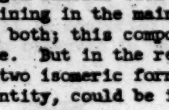
(V)

As has been shown earlier [8], when hydrogen sulfide acts upon β,β-dimethyldivinyl ketone, an unsaturated mercaptoketone first forms, but is later cyclized when heated with sodium acetate in an alcohol solution, forming 2,2-dimethyltetrahydro-1-thiopyran-4-one.

We also reacted hydrogen sulfide with both of the isomers of 5-methyl-1,5-heptadien-4-one (VIII), obtaining in the main the same 2,5,6-trimethyltetrahydro--1-thiopyran-4-one (IX) with both; this compound (IX) was then oxidized to the sulfone (X) with permanganate. But in the reaction described, the thiopyrone (IX) was likewise synthesized in two isomeric forms, one of which (the low-boiling isomer), formed in small quantity, could be isolated only as its semicarbazone.



(VIII)



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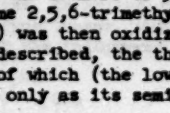
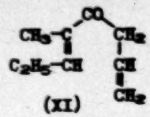


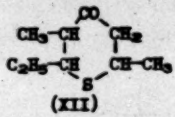
(X)

The action of hydrogen sulfide upon 5-methyl-1,5-octadien-4-one (XI) yielded

2,5-dimethyl-6-ethyltetrahydro-1-thiopyran-4-one (XII), with a yield of about 70%; this was then oxidized to the corresponding sulfone (XIII) by permanganate:



(XI)



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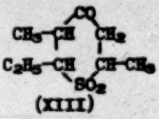
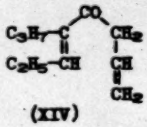
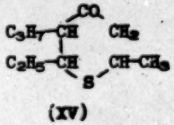


(XIII)

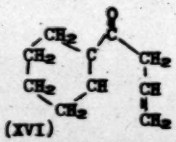
Thiopyrones containing higher aliphatic radicals, as well as thiopyrones of polycyclic structure, can also be synthesized in an analogous fashion. For instance, a yield of 35% of 2-methyl-6-ethyl-5-propyltetrahydro-1-thiopyran-4-one (XV) was obtained by reacting hydrogen sulfide with 5-propyl-1,5-octadien-4-one (XIV), and the action of hydrogen sulfide on allyl-Δ'-cyclohexenyl ketone (XVI), synthesized 2-methylhexahydro-1-thiochroman-4-one (XVII) with a yield of 58%:



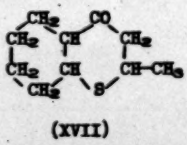
(XIV)



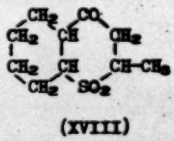
(XV)



(XVI)



(XVII)

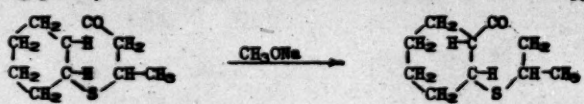


(XVIII)

A bicyclic thiopyrone (XVII) was synthesized in two isomeric crystalline forms, which yielded the corresponding sulfones (XVIII) when oxidized by permanganate and formed differing 2,4-dinitrophenylhydrazones. Both isomers of the thiochromanone (XVII) yield the same semicarbazone, as was the case in the thiopyrone (V); it is most probable that this semicarbazone corresponds to the trans isomer.

Similar instances of the isomerization of cis forms of cyclic ketones to their trans form at the instant of forming their semicarbazones have been described in the literature, [10], and have been often observed in our own laboratory as well.

When the cis-isomer, which has a low melting point, is boiled in a dilute solution of sodium methylate, it is converted to the trans isomer, which has a high melting point, as was also observed in the case of the thiopyrone (V).



The cis-trans isomerization of thiochromanones (XVII) depends upon the arrangement of the hydrogen atoms at the junctions of the rings, as is the case in the well-known cis-trans isomers in the α-decalone series [11].

As in the isomerization of carboxylic ketones, we apparently must assume a

keto-enolic mechanism [12] for the cis-trans isomerization of tetrahydro-γ-thiopyrones.

Our endeavor to effect a cis-trans isomerization of the sulfones (XVIII) was fruitless, notwithstanding our having employed a more highly concentrated solution of sodium methylate (0.15% sodium in methanol) than was used to isomerize the sulfones (VI) (0.06% sodium in methanol). The sulfones (XVIII) decompose when they are boiled with still higher concentrations of sodium methylate.

The tetrahydro-γ-thiopyrones described in this paper are colorless liquids with a characteristic odor, which form semicarbazones with ease, as a rule. The sulfones are colorless crystals with no odor at all.

EXPERIMENTAL

All the vinyl allyl ketones were prepared by hydrating the corresponding divinylacetylenic hydrocarbons in aqueous solutions of methanol in the presence of sulfuric acid and mercuric sulfate, as has been described previously [2].

2-Methyltetrahydro-1-thiopyran-4-one (II)

6 g of anhydrous sodium acetate was dissolved in 200 ml of 96% alcohol, the flask was immersed in ice water, and hydrogen sulfide was passed through the solution for 20 minutes. Then 37 g of vinyl allyl acetone (b.p. 42-45° at 18 mm; n_D^{20} 1.4690) was added during the course of 2.5 hours while the current of hydrogen sulfide continued to flow uninterruptedly. After that, the hydrogen sulfide was passed through the reaction mixture for another 1.5 hours at 0°, and the mixture was then set aside to stand overnight. The next day 4 g of sodium acetate was added, and the solution was boiled for 7 hours. The alcohol was driven off over a water bath, water was added, and the product was extracted with ether, washed with water, dried with magnesium sulfate, and distilled in vacuum. This yielded 14 g of 2-methyltetrahydro-1-thiopyran-4-one (II) with a b.p. of 89-90° at 15 mm; n_D^{19} 1.5052. The residue consisted of 22 g of a polymer that decomposed upon fractionation.

Pure 2-methyltetrahydro-1-thiopyran-4-one is a colorless liquid with a characteristic odor:

B.p. 82.5° at 12 mm; n_D^{20} 1.5094; d_4^{20} 1.0877; MR_D found 35.77; calc. 35.69.
4.052 mg substance: 7.237 mg $BaSO_4$.
6.812 mg substance: 12.235 mg $BaSO_4$.
Found %: S 24.59, 24.67.
$C_6H_{10}OS$. Calculated %: S 24.63.

The semicarbazone of 2-methyltetrahydro-1-thiopyran-4-one fused at 168° after recrystallization from methanol.

4.810 mg substance: 0.959 ml N_2 (24°, 746 mm).
4.615 mg substance: 0.913 ml N_2 (24°, 745 mm).
Found %: 22.49, 22.29.
$C_7H_{13}ON_3S$. Calculated %: N 22.55.

Sulfone of 2-Methyltetrahydro-1-thiopyran-4-one (III)

3 g of the thiopyranone (II) was dissolved in 30 ml of acetone, and 14 ml of 10% sulfuric acid and 5 g of powdered potassium permanganate were gradually added to the solution with constant water-cooling and constant stirring. Oxidation was complete after 1.5 hours. The manganese dioxide formed was filtered out and washed repeatedly with hot water. The aqueous solution was evaporated; it yielded 3 g of the crystalline sulfone. The sulfone of 2-methyltetrahydro-1-thiopyran-4-one

(III) consists of colorless, odorless crystals with a m.p. of 80° (from methanol and benzene).

3.485 mg substance: 2.155 ml 0.02 N I_2.
3.310 mg substance: 2.043 ml 0.02 N I_2.
Found %: S 19.83, 19.79.
$C_8H_{10}O_3S$. Calculated %: S 19.77.

2,5-Dimethyltetrahydro-1-Thiopyran-4-one (V)

a) 3.5 g of anhydrous sodium acetate was dissolved in 140 ml of 96% alcohol, the flask was immersed in ice water,* and hydrogen sulfide was passed through the solution for 20 minutes. Then 18 g of allyl isopropenyl ketone (b.p. 51-52° at 16 mm; n_D^{20} 1.4712), was gradually added while the current of hydrogen sulfide continued to flow. After that, the current of hydrogen sulfide was allowed to flow for another 2 hours at 0°. The next day 22 g of sodium acetate was added, and the reaction mixture was boiled for 14 hours with a reflux condenser. The mercaptan odor disappeared. Most of the alcohol was driven off over a water bath, the residue being diluted with water, yielding 16 g of the crystalline thiopyrone (V). After the crystals had been separated out, the product was extracted with ether, washed with water, dried with sodium sulfate, and fractionated in vacuum. This yielded another 7.5 g of the substance, with a b.p. of 87-88° at 13 mm, which crystallized partially in the receiver. The crystals were separated from the mother liquor and combined with those previously obtained. The aggregate yield of the crystalline trans-thiopyrone (V) was 16 g after recrystallization, or 68% of the theoretical.

Trans-2,5-dimethyltetrahydro-1-thiopyran-4-one consists of colorless crystals with a m.p. of 71° (from alcohol or petroleum ether) that have a characteristic acrid odor. They do not exhibit the sulfhydryl group reaction with nitric acid.

0.1489 g substance: 15.6 g benzene: Δt 0.328°.
0.1034 g substance: 15.6 g benzene: Δt 0.228°.
Found : M 149.3, 149.1.
$C_7H_{12}OS$. Calculated : M 144.2.

5.926 mg substance: 9.630 mg $BaSO_4$.
5.330 mg substance: 8.609 mg $BaSO_4$.
Found %: S 22.31, 22.18.
$C_7H_{12}OS$. Calculated %: S 22.23.

The semicarbazone of trans-2,5-dimethyltetrahydro-1-thiopyran-4-one fused at 173-174° after recrystallization from alcohol.

3.030 mg substance: 0.544 ml N_2 (24°, 751 mm).
3.770 mg substance: 0.674 ml N_2 (24°, 751 mm).
Found %: N 20.39, 20.31.
$C_8H_{15}ON_3S$. Calculated %: N 20.88.

5.872 mg substance: 10.277 mg CO_2; 3.942 mg H_2O.
3.950 mg substance: 6.905 mg CO_2; 2.689 mg H_2O.
Found %: C 47.76, 47.70; H 7.51, 7.62.
$C_8H_{15}ON_3S$. Calculated %: C 47.75; H 7.51.

The 2,4-dinitrophenylhydrazone of trans-2,5-dimethyltetrahydrothiopyran-4-one fused at 188° after recrystallization from alcohol (straw-yellow needles).

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* The reaction can also be effected at room temperature, without cooling, but the yield of the thiopyranone is then somewhat lower (63%).

3.050 mg substance: 0.465 ml N_2 (20°, 756 mm).
4.510 mg substance: 0.691 ml N_2 (20°, 756 mm).
Found %: N 17.61, 17.50.
$C_{13}H_{16}O_4N_4S$. Calculated %: N 17.33.

b) Three other tests were made with an aggregate quantity of 147 g of the initial allyl isopropenyl ketone, under conditions resembling those described. Vacuum distillation and freezing of the liquid fractions yielded 91 g of the crystalline trans-thiopyrone with a m.p. of 71° (from methanol).

The liquid fractions were combined, and after repeated vacuum fractionation, they yielded 16.5 g of a liquid mixture of the cis and trans isomers of 2,5-dimethyltetrahydro-1-thiopyran-4-one:

B.p. 94° at 17 mm; n_D^{18} 1.5038; d_4^{20} 1.0851; MR_D found 39.32; calc. 40.31.
4.669 mg substance: 3.093 ml 0.02 N I_2.
2.932 mg substance: 1.981 ml 0.02 N I_2.
Found %: S 21.37, 21.30.*
$C_7H_{12}OS$. Calculated %: S 22.23.

Moreover, vacuum fractionation also yielded 16 g of 1,3-dimethylcyclopenten-5-one, with a b.p. of 162-165°, n_D^{23} 1.4651, formed as a result of the cyclization of the allyl isopropenyl ketone. Its 2,4-dinitrophenylhydrazone fused at 207° and exhibited no depression when mixed with a standard sample.

[illegible] mixture of thiopyrones (V), [illegible] alcohol) [illegible] depression [illegible]

The semicarbazone, prepared from the liquid mixture of thiopyrones (V), fused at 171-172° (from alcohol) and exhibited no depression when mixed with the semicarbazone of the crystalline isomer described above.

3.854 mg substance: 0.696 ml N_2 (21°, 746 mm).
3.710 mg substance: 0.675 ml N_2 (21°, 746 mm).
Found %: N 20.58, 20.74.
$C_8H_{15}ON_3S$. Calculated %: N 20.88.

The 2,4-dinitrophenylhydrazones prepared from the liquid mixture of the thiopyrones (V) contained both isomers; the latter were separated by fractional crystallization from alcohol. This yielded, in addition to the 2,4-dinitrophenylhydrazone of the trans-thiopyrone with a m.p. of 188° already described, the 2,4-dinitrophenylhydrazone of the cis isomer of the thiopyrone (V) as orange lamellae with a m.p. of 142-143°.

3.420 mg substance: 0.557 ml N_2 (16°, 741 mm).
Found %: N 18.00.
$C_{13}H_{16}O_4N_4S$. Calculated %: N 17.33.

Cis-Trans Isomerization of 2,5-Dimethyltetrahydro-1-thiopyran-4-one

12.5 g of the liquid isomer of the thiopyrone (V) (b.p. 104-105° at 23 mm; n_D^{18} 1.5035) was boiled for 5 hours in a solution of 50 ml of methanol containing 0.25 g of sodium. After the methanol had been driven off in vacuum, we recovered 11 g of the crystalline isomer of the thiopyrone (V), fusing at 71° after recrystallization from alcohol and exhibiting no depression when mixed with the sample described above.

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*The drop in the sulfur content in the liquid isomer is apparently due to a trace of 1,3-dimethyl-1-cyclopenten-5-one.

Sulfone of the Crystalline Isomer of 2,5-Dimethyltetrahydro-1-thiopyran-4-one (VI)

6 g of the thiopyrone (m.p. 71°) was dissolved in 130 ml of acetone, after which 26 ml of 10% sulfuric acid and 8.8 g of powdered potassium permanganate were gradually added with vigorous stirring and water-cooling. Oxidation was complete in 2 hours.

The manganese dioxide formed was filtered out and washed repeatedly with hot water; the filtrate and the wash waters were combined and extracted with ether, but nothing could be recovered from the extract. The aqueous solution was evaporated, yielding 4 g of the sulfone of the solid isomer of 2,5-dimethyltetrahydro-1-thiopyran-4-one (VI) as colorless, odorless crystals with a m.p. of 138° (from ethyl alcohol).

5.532 mg substance: 7.169 mg $BaSO_4$.
5.416 mg substance: 7.029 mg $BaSO_4$.
Found %: S 17.79, 17.82.
$C_7H_{12}O_3S$. Calculated %: S 18.19.

4.107 mg substance: 7.205 mg CO_2; 2.480 mg H_2O.
5.120 mg substance: 8.970 mg CO_2; 3.120 mg H_2O.
Found %: C 47.87, 47.81; H 6.75, 6.82.
$C_7H_{12}O_3S$. Calculated %: C 47.71; H 6.86.

Sulfone of the Liquid Isomer of 2,5-Dimethyltetrahydro-1-thiopyran-4-one (VI)

4 g of a liquid mixture of the thiopyrones (V) was dissolved in 75 ml of acetone, and 6.2 g of powdered potassium permanganate and 22 ml of 10% sulfuric acid were gradually added to the solution with vigorous stirring and water-cooling.

The manganese dioxide that formed was filtered out and washed repeatedly with hot water. The filtrate and the wash waters were combined together, neutralized with soda, and extracted with ether. The ether solution was dried with sodium sulfate, and after the ether had been driven off, 0.2 g of the sulfone of the liquid isomer of 2,5-dimethyltetrahydro-1-thiopyran-4-one (VI), with a m.p. of 103-104° (from alcohol) was recovered.

3.147 mg substance: 1.780 ml 0.02 N I_2.
3.848 mg substance: 2.159 ml 0.02 N I_2.
Found %: S 18.14, 17.99.
$C_7H_{12}O_3S$. Calculated %: S 18.19.

The aqueous solution was evaporated to dryness, and the residue was extracted with alcohol. Fractional crystallization of the alcohol solution yielded 0.8 g of the sulfone of the solid isomer of the thiopyrone (V), with a m.p. of 138°, which caused no depression when mixed with the sample described above.

Cis-Trans Isomerization of Sulfones of 2,5-Dimethyltetrahydro-1-thiopyran-4-one

0.04 g of the sulfone of the cis isomer, with a m.p. of 103-104°, was boiled for 2 hours in a solution of 0.3 ml of methanol containing 0.06% of sodium. The alcohol was driven off, and the residue yielded the sulfone of the trans isomer, with a m.p. of 138°, which exhibited no depression when mixed with a known sample.

2-Methylhexane-1,5-dithiol-3-one (VII)

Hydrogen sulfide was passed through an ice-chilled solution of 0.4 g of sodium acetate in 150 ml of acetone and 1.5 ml of water for 20 minutes. Then the

solution was stirred and the current of hydrogen continued for an hour while 14.5 g of allyl isopropenyl ketone was added drop by drop. After this, 0.5 g of pyrogallol was added to the solution, and the hydrogen sulfide was passed through the solution for another 3 hours at 0°.

The next day the acetone was driven off in vacuum at a bath temperature of 30°. The residue was dissolved in ether, and the ether solution was washed with water and dried with sodium sulfate.

Repeated vacuum fractionation yielded 7 g of 2-methylhexane-1,5-dithiol-3-one (VII):

B.p. 98.5° at 4.5 mm; $n_D^{20°}$ 1.5120; $d_4^{20°}$ 1.0755; MR_D found 49.75; calculated 50.06.

0.2384 g substance; 15.38 g of benzene: Δt 0.458°.
0.3369 g substance; 15.38 g of benzene: Δt 0.632°.
Found: M 173.6, 174.5.
$C_7H_{12}OS_2$. Calculated: M 178.3.

3.060 mg substance: 7.895 mg $BaSO_4$.
3.560 mg substance: 9.217 mg $BaSO_4$.
Found %: S 35.43, 35.56.
$C_7H_{14}OS_2$. Calculated %: S 35.90.

2-Methylhexane-1,5-dithiol-3-one is a colorless liquid with a characteristic repellent odor. It exhibits a marked sulfhydryl reaction with nitric acid. When it is reacted with mercurous cyanide and naphthyl isocyanate, glassy noncrystalline products are formed.

Tserevitnikov sulfhydryl-group determination:

0.0584 g substance: 14.42 ml CH_4 (18°, 772 mm).
0.0719 g substance: 17.70 ml CH_4 (18°, 772 mm).
Found %: SH 34.89, 34.79.
$C_7H_{12}O(SH)_2$. Calculated %: SH 37.09.

Cyclization of 2-Methylhexane-1,5-dithiol-3-one to 2,5-Dimethyltetrahydro-1-thiopyran-4-one

2.2 g of the dithiol (VII) and 1.9 g of sodium acetate were dissolved in 20 ml of 96% alcohol. The solution was boiled for 4.5 hours with a reflux condenser, hydrogen sulfide being liberated with special violence during the first half hour. After the alcohol had been driven off and the residue diluted with water, we recovered 1 g of crystals of 2,5-dimethyltetrahydro-1-thiopyran-4-one. The aqueous solution was extracted with ether, the ether extract was dried with magnesium sulfate, the ether was driven off, and the residue was distilled in vacuum. This yielded another 0.5 g of the thiopyrone (V), with a b.p. of 86° at 14 mm, which crystallized upon cooling.

After recrystallization from alcohol, the synthesized 2,5-dimethyltetrahydro-1-thiopyran-4-one fused at 71° and exhibited no depression when mixed with the preceding sample.

2,3,6-Trimethyltetrahydro-1-thiopyran-4-one (IX)

This synthesis was effected with both the low-boiling and the high-boiling isomers of 5-methyl-1,5-heptadien-4-one. The result was, by and large, the same 2,3,6-trimethyltetrahydro-1-thiopyran-4-one.

a) 4 g of anhydrous sodium acetate was dissolved in 155 ml of 96% alcohol, and hydrogen sulfide was passed through the ice-chilled mixture for 20 minutes.

Then 27 g of the low-boiling isomer of 5-methyl-1,5-heptadien-4-one (b.p. 64-65° at 14 mm; n_D^{18} 1.4720), was gradually added over the course of 40 minutes while the current of hydrogen sulfide continued to pass through the solution without interruption. The hydrogen sulfide was passed through for another 2 hours at 0°, and the product was set aside to stand overnight. The next day 3 g of sodium acetate was added to the solution, and the reaction mixture was boiled for 5 hours with a reflux condenser. The alcohol was driven off, and the residue was treated in the usual manner.

Fractionation yielded 21.7 g of 2,3,6-trimethyltetrahydro-1-thiopyran-4-one (IX), with a b.p. of 84-86° at 9 mm; n_D^{18} 1.4960 (yield = 64% of the theoretical).

b) 37 g of anhydrous sodium acetate was dissolved in 1.5 liters of 96% alcohol, the flask was immersed in ice water, and 340 g of the high-boiling isomer of 5-methyl-1,5-heptadien-4-one (b.p. 65-68° at 8 mm; n_D^{18} 1.4815) was gradually added during 2.5 hours while hydrogen sulfide was passed through the solution uninterruptedly. The hydrogen sulfide was passed through for another 21 hours, and then 35 g of sodium acetate was added, and the solution boiled for 7 hours. The product was then given the usual treatment.

Repeated fractionation yielded 238 g of 2,3,6-trimethyltetrahydro-1-thiopyran-4-one, with a b.p. of 79-80° at 8 mm; n_D^{20} 1.4960.

In addition, we recovered 80 g of heads, with a b.p. of 77-79° at 8 mm; n_D^{18} 1.4915, which consisted of a mixture of two isomers of 2,3,6-trimethyltetrahydro-1-thiopyran-4-one (vide infra). The polymeric residue after fractionation totaled about 100 g.

2,3,6-Trimethyltetrahydro-1-thiopyran-4-one is a colorless liquid with a characteristic odor:

B.p. 79° at 8 mm; n_D^{20} 1.4963; d_4^{20} 1.0288; MR_D found 44.97; calculated 44.92.

3.241 mg substance: 4.710 mg $BaSO_4$.
7.290 mg substance: 10.885 mg $BaSO_4$.
Found %: S 19.95, 20.50.
$C_8H_{14}OS$. Calculated %: S 20.26.

The semicarbazone of 2,3,6-trimethyltetrahydro-1-thiopyran-4-one fuses at 173° (from alcohol).

3.040 mg substance: 0.529 ml N_2 (23°, 727 mm).
3.170 mg substance: 0.542 ml N_2 (24°, 741 mm).
Found %: N 19.15, 19.16.
$C_9H_{17}ON_3S$. Calculated %: N 19.53.

The overhead distillate (b.p. 76-77° at 7 mm; n_D^{18} 1.4915), which consisted, as we have said, of a mixture of two isomers of 2,3,6-trimethyltetrahydro-1-thiopyran-4-one, yielded two semicarbazones upon fractional distillation: one with a m.p. of 173°, which was identical with the semicarbazone described above (exhibited no depression when mixed with a test sample), and the other with a m.p. of 135° (from alcohol).

2.60 mg substance: 0.443 ml N_2 (20°, 746 mm).
3.16 mg substance: 0.546 ml N_2 (22°, 746 mm).
Found %: N 19.44, 19.62.
$C_9H_{17}ON_3S$. Calculated %: N 19.53.

Sulfone of 2,3,6-Trimethyltetrahydro-1-thiopyran-4-one (X)

6 g of the thiopyrone (IX) was dissolved in 125 ml of acetone, and 8.8 g

of powdered potassium permanganate and 25 ml of 10% sulfuric acid were gradually added to the solution while the latter was vigorously stirred and water-cooled. Oxidation was complete after 2 hours.

The manganese dioxide that formed was filtered out and repeatedly washed with hot water. The filtrate and the wash waters were extracted with ether. The ether solution was dried with sodium sulfate, the ether was driven off, and the residue was distilled in vacuum. This yielded 3 g of the sulfone (I), which distils with decomposition at 118-122° at 1.5 mm; n_D^{18} 1.5042.

The sulfone crystallizes upon standing, forming colorless crystals, which fused at 128° after recrystallization from alcohol.

3.928 mg substance: 4.803 mg $BaSO_4$.
3.189 mg substance: 3.868 mg $BaSO_4$.
Found %: S 16.80, 16.66.
$C_8H_{14}O_3S$. Calculated %: S 16.84.

4.788 mg substance: 8.850 mg CO_2; 3.212 mg H_2O.
4.070 mg substance: 7.510 mg CO_2; 2.630 mg H_2O.
Found %: C 50.44, 50.36; H 7.50, 7.23.
$C_8H_{14}O_3S$. Calculated %: C 50.50; H 7.42.

2,5-Dimethyl-6-ethyltetrahydro-1-thiopyran-4-one (XII)

6.3 g of anhydrous sodium acetate was dissolved in 250 ml of 96% alcohol, the flask was immersed in ice water, and hydrogen sulfide was passed through the solution for 20 minutes. Then the hydrogen sulfide was passed through the solution uninterruptedly for another hour while 44 g of 5-methyl-1,5-octadien-4-one (b.p. 72-80° at 13 mm; n_D^8 1.4735 [13]) was added. After this, the hydrogen sulfide was passed through for two more hours at 0°. The next day 5 g of sodium acetate was added, and the reaction mass was boiled for 5 hours with a reflux condenser.

Treatment of the reaction product in the usual manner yielded 36 g of 2,5-dimethyl-6-ethyltetrahydro-1-thiopyran-4-one (XII), with a b.p. of 102-105° at 12 mm; n_D^{17} 1.4942, which corresponds to 67% of the theoretical yield.

2,5-Dimethyl-6-ethyltetrahydro-1-thiopyran-4-one is a colorless liquid with a characteristic acrid odor:

B.p. 81° at 4.5 mm; n_D^{20} 1.4938; d_4^{20} 1.0150; MR_D found 49.39; calculated 49.54.

0.1633 g substance: 15.4 g of benzene: Δt 0.310°.
0.3159 g substance: 15.4 g of benzene: Δt 0.600°.
Found M 173.5, 173.4.
$C_9H_{16}OS$. Calculated: M 172.28.

3.200 mg substance: 4.299 mg $BaSO_4$.
4.350 mg substance: 5.830 mg $BaSO_4$.
Found %: S 18.45, 18.40.
$C_9H_{16}OS$. Calculated %: S 18.61.

The semicarbazone of 2,5-dimethyl-6-ethyltetrahydro-1-thiopyran-4-one fuses at 150.5° (from alcohol).

3.67 mg substance: 0.583 ml N_2 (22°, 751 mm).
3.31 mg substance: 0.521 ml N_2 (24°, 751 mm).
Found %: N 18.12, 17.95.
$C_{10}H_{19}ON_3S$. Calculated %: N 18.31.

Sulfone of 2,5-Dimethyl-6-ethyltetrahydro-1-thiopyran-4-one (XIII)

4 g of the thiopyrone (XII) was dissolved in 85 ml of acetone, and 5.8 g of powdered potassium permanganate, and 15 ml of 10% sulfuric acid were gradually added to the solution with vigorous stirring and water-cooling. Oxidation was complete in 2 hours.

The manganese dioxide formed was filtered out and washed repeatedly with hot water, after which the filtrate and the wash waters were extracted with ether. The ether solution was dried with sodium sulfate, and after the ether had been driven off, the residue was distilled in vacuum. This yielded 2 g of a thick yellow substance with a b.p. of 133° at 4 mm; n_D^{17} 1.4960; We were unable to crystallize the synthesized sulfone, (XIII).

The semicarbazone of the sulfone consists of colorless crystals that fuse at 189° (from alcohol).

4.995 mg substance: 0.706 ml N_2 (22°, 746 mm).
5.010 mg substance: 0.708 ml N_2 (23°, 746 mm).
Found %: N 16.06, 16.00.
$C_{10}H_{19}O_3N_3S$. Calculated %: N 16.07.

2-Methyl-5-propyl-6-ethyltetrahydro-1-thiopyran-4-one (XV)

4 g of anhydrous sodium acetate was dissolved in 150 ml of 96% alcohol, and hydrogen sulfide was passed through the ice-water-chilled solution for 20 minutes. Then hydrogen sulfide was passed through the solution uninterruptedly for 40 minutes while 20.5 g of 5-propyl-1,5-octadien-4-one (b.p. 86-88° at 6 mm; n_D^{23} 1.4880) [14] was added. Afterwards, hydrogen sulfide was passed through for another 5 hours at 0°. The next day 3 g of sodium acetate was added, and the reaction mass was boiled for 6 hours with a reflux condenser. The alcohol was driven off in vacuum, and the residue received the usual treatment.

Fractionation in vacuum yielded 8.7 g of 2-methyl-5-propyl-6-ethyltetrahydro-1-thiopyran-4-one (XV) as a colorless liquid with a characteristic acrid odor:

B.p. 113° at 8 mm; n_D^{20} 1.4892; d_4^{20} 0.9864; MR_D found 58.50; calculated 58.77.
0.1583 g substance: 15.3 g of benzene: Δt 0.269°.
0.2439 g substance: 15.3 g of benzene: Δt 0.415°.
Found : M 197.1, 196.8.
$C_{11}H_{20}OS$. Calculated : M 200.33.
3.448 mg substance: 1.710 ml 0.02 N I_2.
3.479 mg substance: 1.730 ml 0.02 N I_2.
Found %: S 15.90, 15.94.
$C_{11}H_{20}OS$. Calculated %: S 16.00.

2-Methylhexahydro-1-thiopyran-4-one (XVII)

a) 13.6 g of sodium acetate was dissolved in 300 ml of 96% alcohol, the flask was immersed in ice water, and hydrogen sulfide was passed through the solution for 20 minutes. Then hydrogen sulfide was passed through the solution uninterruptedly for 1.5 hours while 97 g of allyl-Δ¹-cyclohexenyl ketone (XVI) (b.p. 97° at 5 mm; n_D^{20} 1.5165) was added. Afterwards, hydrogen sulfide was passed through for another 12 hours at 0°. The reaction mass was then boiled for 6 hours with a reflux condenser. The alcohol was driven off, and the residue was diluted with water. The 30 g of crystals of 2-methylhexahydro-1-thiopyran-4-one (XVII) that separated out was removed. The filtrate was extracted with ether, the ether solution dried with sodium sulfate, the ether driven off, and the residue distilled in vacuum.

Repeated fractionation and freezing enabled us to recover another 4 g of the crystalline thiochromanone (XVII) and 36 g of a liquid mixture of isomers, with a b.p. of 112-115°, at 6 mm (overall yield = 58% of the theoretical). The trans isomer of 2-methylhexahydro-1-thiopyran-4-one, which has the higher melting point, consists of colorless crystals with a m.p. of 77.5° (from methanol), which had a slight characteristic odor. They give a negative reaction for the sulfhydryl group.

0.0487 g substance: 15.9 g of benzene: Δt 0.083°.
0.0990 g substance: 15.9 g of benzene: Δt 0.180°.
Found: M 189.3, 177.4.
$C_{10}H_{16}OS$. Calculated: M 184.3.
3.354 mg substance: 4.249 mg $BaSO_4$.
6.311 mg substance: 7.926 mg $BaSO_4$.
Found %: S 17.40, 17.25.
$C_{10}H_{16}OS$. Calculated %: S 17.39.

The semicarbazone of the high-melting trans-thiochromanone (XVII) fuses at 203-203.5° (from methanol).

3.400 mg substance: 0.507 ml N_2 (18°, 753 mm).
3.640 mg substance: 0.549 ml N_2 (20°, 754 mm).
Found %: N 17.33, 17.43.
$C_{11}H_{19}ON_3S$. Calculated %: N 17.42.

The 2,4-dinitrophenylhydrazone of the trans-thiochromanone (XVII) fuses at 223° (from a mixture of benzene and petroleum ether).

3.800 mg substance: 0.510 ml N_2 (22°, 758 mm).
3.380 mg substance: 0.453 ml N_2 (21°, 762 mm).
Found %: N 15.50, 15.60
$C_{16}H_{20}O_4N_4S$. Calculated %: N 15.37.

The liquid mixture of isomers of the thiochromanone (XVII) was subjected to further vacuum distillation, which yielded a substance with a b.p. of 111° at 5 mm; n_D^{20} 1.5270; d_4^{20} 1.0578. The product gives a negative reaction for the sulfhydryl group with nitric acid, mercurous cyanide, sodium nitroprusside, and methylmagnesium iodide (active hydrogen, Tserevitinov reaction).

MR_D found 53.56; calculated 51.96.
0.199 g substance; 17.85 g of benzene: Δt 0.308°
0.315 g substance; 17.85 g of benzene: Δt 0.545°.
Found: M 185.4, 179.8.
$C_{10}H_{16}OS$. Calculated: M 184.3.
3.200 mg substance: 4.030 mg $BaSO_4$.
3.405 mg substance: 4.339 mg $BaSO_4$.
Found %: S 17.30, 17.51.
$C_{10}H_{16}OS$. Calculated %: S 17.39.

3 g of the liquid fraction yielded a mixture of 2,4-dinitrophenylhydrazones, from which the 2,4-dinitrophenylhydrazones of the cis- and trans-thiochromanones (XVII), with m.p. of 184° and 223°, respectively, were recovered by fractional crystallization. Moreover, we isolated a negligible quantity of a colorless substance with a m.p. of 215° as small needles, but we did not establish its structure.

Analysis indicated a nitrogen content of 7.42% and a sulfur content of 17.12%.

b) We took 120 g of allyl-Δ'-cyclohexenyl ketone, 26 g of sodium acetate, and 500 ml of alcohol. After the mass had been reacted with hydrogen sulfide, the reaction mass was boiled for 32 hours with a reflux condenser. The rest of the

experiment was similar to the preceding one. This yielded 50 g of a mixture of the thiochromanones (XVII), with a m.p. of 62-65° (from methanol) and 60 g of liquid fractions with a b.p. of 117-125° at 7 mm; n_D^{18} 1.5190.

The trans isomer, with a m.p. of 77.5°, was isolated from the mixture of thiochromanones by means of crystallization from methanol and petroleum ether.

Vacuum distillation of the liquid fractions, followed by freezing, yielded 27 g of crystals with a m.p. of 42-47°. Fractional crystallization of this mixture from methanol yielded 1.5 g of the cis isomer of 2-methylhexahydro-1-thiochroman-4-one, which crystallizes as colorless needles with a m.p. of 65°.

3.744 mg substance: 2.024 ml 0.02 N I_2.
4.640 mg substance: 2.513 ml 0.02 N I_2.
Found %: S 17.33, 17.36.
$C_{10}H_{16}OS$. Calculated %: S 17.39.

A test sample mixed with the trans isomer (m.p. 77.5°) fused at 52-57°).

The semicarbazone of the cis-thiochromanone (XVII) fused at 202.5-203° and exhibited no depression when mixed with the semicarbazone of the trans isomer described above (the mixture of semicarbazones fused at 199-201°).

The 2,4-dinitrophenylhydrazone prepared from the pure cis-thiochromanone (XVII) fuses at 184°.

3.770 mg substance: 0.505 ml N_2 (22°, 758 mm).
Found %: N 15.46.
$C_{16}H_{20}O_4N_4S$. Calculated %: N 15.37.

c) An experiment with 87 g of allyl-Δ'-cyclohexenyl ketone was run under similar conditions. The reaction liquid was boiled for 16 hours with a reflux condenser. Treatment was as usual. The yield was 44 g of crystal with a m.p. of 68-70°, 27 g of liquid fractions with a b.p. of 109-123° at 6 mm, n_D^{21} 1.5200, and 5.5 g of overhead fractions. The overhead fractions were removed. The liquid mixture of isomers and the crystals were combined together and dissolved in 350 ml of methanol containing 1 g of sodium. The solution was boiled for 3 hours with a reflux condenser. After the methanol had been driven off, we recovered 65.6 g of trans-2-methylhexahydro-1-thiopyran-4-one, with a m.p. of 76-77°, or 62% of the theoretical yield.

Cis-Trans Isomerization of 2-Methyl-hexahydro-1-thiochroman-4-one

a) 0.2 g of the cis-thiochromanone (m.p. 63-65°) was boiled for 2 hours in a solution of 1 ml of methanol containing 3 mg of sodium. When the solution cooled, crystals with a m.p. of 76-77° separated out.

They fused at 77-77.5° after recrystallization from petroleum ether and exhibited no depression in a test sample mixed with the trans-thiochromanone (XVII) described above.

b) 16 g of a liquid mixture of the isomers was boiled for 2 hours in a solution of 80 ml of methanol containing 0.24 g of sodium. When the solution cooled, 6.3 g of crystals of the trans-thiochromanone (XVII), with a m.p. of 76-77°, settled out, another 7.8 g of crystals, which also fused at 75-76° (from methanol) and exhibited no depression when mixed with the preceding sample, being recovered by evaporating most of the solvent.

c) When 2 g of the trans-thiochromanone (XVII) (b.p. 77°), dissolved in 15 ml of methanol containing 0.015 g of sodium, was boiled for 6 hours, the product underwent no change and was recovered intact.

Sulfone of 2-Methylhexahydro-1-thiochroman-4-one (XVIII)

a) 5 g of the trans-thiochromanone (m.p. 77.5°) was dissolved in 50 ml of acetone, and 17.6 g of 10% sulfuric acid was added to the solution, after which 5.7 g of permanganate was added with stirring and water-cooling.

The reaction product was given the usual treatment. This yielded 4.5 g of the sulfone of the trans-thiochromanone (XVIII) as colorless crystals with a m.p. of 157-158° (from alcohol).

3.272 mg substance: 5.676 mg $BaSO_4$
3.299 mg substance: 3.507 mg $BaSO_4$
Found %: S 14.78, 14.60.
$C_{10}H_{18}O_3S$. Calculated %: S 14.81.

b) 0.35 g of the cis-thiochromanone (m.p. 64°) was dissolved in 6 ml of acetone, and 1.32 ml of 10% sulfuric acid and 0.42 g of potassium permanganate were added to the solution. The reaction product was given the usual treatment. This yielded 0.270 g of the sulfone of the cis-thiochromanone (XVIII) as lustrous platelets with a m.p. of 144° (from alcohol).

3.793 mg substance: 1.731 ml 0.02 N I_2.
Found %: S 14.64
$C_{10}H_{18}O_3S$. Calculated %: S 14.81.

c) 7 g of a liquid mixture of the isomers (b.p. 111° at 5 mm; n_D^{20} 1.5270) was dissolved in 80 ml of acetone. 26.4 ml of 10% sulfuric acid and 8.5 g of permanganate were added to the solution. Oxidation was complete in 2 hours. 6 g of a crystalline mixture of the sulfones was recovered. The sulfone of the cis isomer, with a m.p. of 144-144.5°, was precipitated by adding petroleum ether to a benzene solution of the mixture of sulfones. It exhibited no depression when mixed with the preceding sample.

The sulfone of the trans isomer, with a m.p. of 157°, was isolated from the mother liquor; it too, exhibited no depression when mixed with the preceding sample.

The sulfones were freed from impurities by heating them with a 0.012% solution of sodium methylate.

Boiling the Sulfones (XVIII) with Dilute Solutions of Sodium Methylate

a) 130 mg of the (XVIII), m.p. 144°, was boiled for 3 hours in a solution of 5 ml of methanol containing 0.15% of sodium. After the alcohol had been driven off, the residue yielded a sulfone contaminated with decomposition products. The m.p. after recrystallization was 144°. The test sample exhibited no depression when mixed with the initial sulfone.

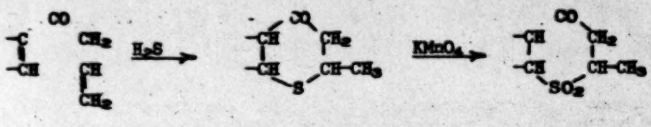
b) 200 mg of the sulfone (XVIII), m.p. 157°, was boiled for 1.5 hours in 10 ml of methanol containing 0.15% of sodium. After the alcohol had been driven off, we recovered a sulfone with a m.p. of 155°. A test sample mixed with the initial sulfone fused at 156-157°.

The sulfones decomposed appreciably when the concentration of sodium in the solution was increased or when heating was prolonged.

SUMMARY

1. The action of hydrogen sulfide upon vinyl allyl ketones in an alcohol solution in the presence of sodium acetate gives rise to a high yield (about 70%) of various tetrahydro-γ-thiopyrones, which are easily oxidized by potassium

permanganate in acetone solution to the corresponding sulfones.



2. In some instances geometrical isomers of the tetrahydro-γ-thiopyrones are isolated, and the corresponding sulfones and 2,4-dinitrophenylhydrazines are synthesized.

3. The cis isomers, of low melting point, have been transformed into trans isomers, with high melting points, by the action of dilute solutions of sodium methylate.

4. The tetrahydro-γ-thiopyrones are formed via the intermediate formation of mercaptoketones, which are then cyclized to tetrahydro-γ-thiopyrones, as was shown in specialized tests.

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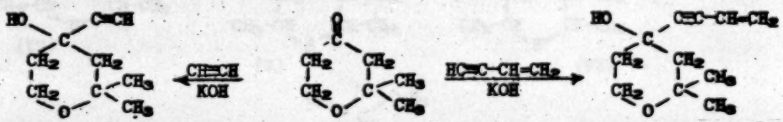
DERIVATIVES OF ACETYLENE

105. RESEARCH ON HETEROCYCLIC COMPOUNDS. XI. SYNTHESIS OF 4-ETHYNYLTETRAHYDROTHIOPYRAN-4-OLS BY THE CONDENSATION OF ACETYLENE WITH TETRAHYDRO-γ-THIOPYRANS

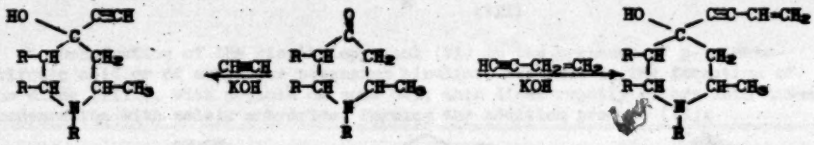
I. N. Nazarov, A. I. Kuznetsova and I. A. Gurvich

Previous papers from our laboratory have described the synthesis of acetylenic and vinylacetylenic alcohols of the piperidine and tetrahydropyran series.

Thus, ethynyl- and vinylethynyltetrahydro-γ-pyranols were synthesized by condensing acetylene and vinylacetylene with tetrahydro-γ-pyrones in the presence of powdered potassium hydroxide [1,2]

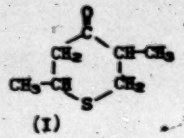


The corresponding ethynyl- and vinylethynyl-γ-hydroxypiperidines were synthesized at high yields by condensing acetylene and vinylacetylene with γ-piperidines [3,4]:

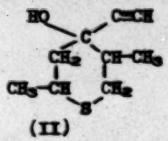


In the present research we effected the synthesis of acetylenic alcohols of the tetrahydro-γ-thiopyran series by condensing acetylene with tetrahydro-γ-thiopyrans in the presence of powdered potassium hydroxide:

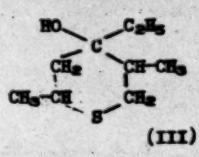
This synthesis proved to be feasible as a result of the simple method for the production of tetrahydro-γ-thiopyrones by the action of hydrogen sulfide upon vinyl allyl ketones developed by us [5]. Condensation of acetylene with 2,5-dimethyltetrahydro-1-thiopyran-4-one (I) resulted in the synthesis, with a yield of 35%, of 2,5-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (II), which was converted into 2,5-dimethyl-4-ethyltetrahydrothiopyran-4-ol (III) by hydrogenation with a Pd catalyst. The latter carbinol was also synthesized, with a yield of 88%, by reacting ethylmagnesium bromide with 2,5-dimethyltetrahydro-1-thiopyran-4-one:



(I)

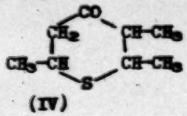


(II)

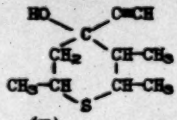


(III)

Condensation of acetylene with 2,3,6-trimethyltetrahydro-1-thiopyran-4-one (IV) resulted in the synthesis, with a yield of some 50%, of 2,3,6-trimethyl-4-ethynyltetrahydrothiopyran-4-ol (V), which was converted into 2,3,6-trimethyl-4-vinyltetrahydrothiopyran-4-ol (VI) by partial hydrogenation with a Pd catalyst and into 2,3,6-trimethyl-4-ethyltetrahydrothiopyran-4-ol (VII) by exhaustive hydrogenation. The latter thiopyranol was also synthesized by reacting ethylmagnesium bromide with the thiopyrone (IV):



(IV)



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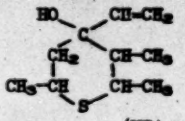
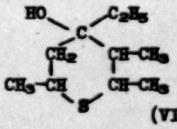
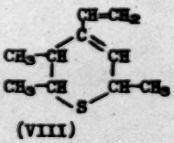


(VI)

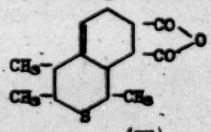


(VII)

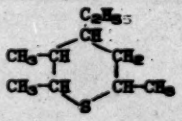
Dehydration of the vinylthiopyranol (VI) in the presence of p-toluenesulfonic acid or of anhydrous potassium bisulfate resulted in the formation of the diene (VIII), with a yield of some 60%; this diene readily enters into diene condensation with maleic anhydride, forming the addition product (IX):



(VIII)



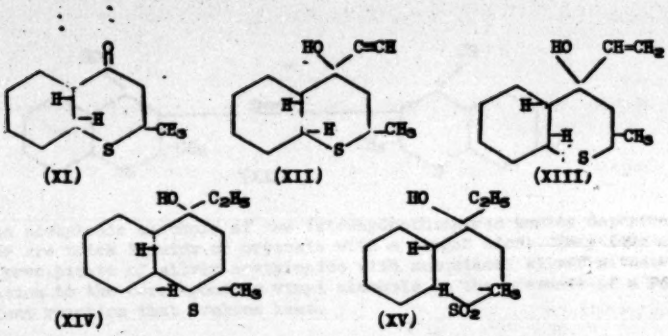
(IX)



(X)

Hydrogenation of the diene (VIII) in the presence of a Pd catalyst yielded 2,3,6-trimethyl-4-ethyltetrahydrothiopyran (X).

Condensation of the trans form of 2-methylhexahydro-1-thiochroman-4-one (XI) with acetylene yielded two crystalline isomers of 2-methyl-4-ethynylthiochroman-4-ol (XII), which were converted into the respective two crystalline isomers of the vinylthiochromanol (XIII) by partial hydrogenation with a Pd catalyst and into two isomeric ethylchromanols (XIV) (liquid and crystalline) by exhaustive hydrogenation:



(XI) (XII) (XIII)

(XIV) (XV)

Oxidation of the ethylchromanols (XIV) by potassium permanganate yielded two isomeric crystalline sulfones (XV).

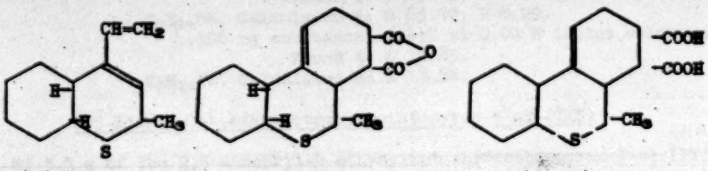
The ethylchromanol (XIV) was likewise synthesized by the action of ethylmagnesium bromide upon the hexahydrothiochromanone (XI), but in this case only a single, solid, isomer was formed.

Arndt also noted the phenomenon of geometrical isomerization in the thiopyranol series [8].

The structure of the two series of trans-thiochromanols (XII, XIII, XIV) and sulfones (XV) synthesized by us corresponds to that of a trans-α-decalol [7]:

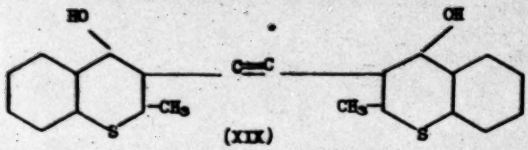
X = S or SO_2; R = CH≡C; CH_2=CH; C_2H_5

Dehydration of vinylthiochromanol (XIII) with p-toluene sulfonic acid or potassium bisulfate results in the formation of about 50% of the diene (XVI); condensation of the latter with maleic anhydride yields the anhydride (XVII), and saponification of the latter produces the acid (XVIII):



(XVI) (XVII) (XVIII)

Condensation of acetylene with the thiochromanone (XI) yielded the acetylenic glycol (XIX) in addition to the acetylenic alcohol (XII).



(XIX)

The acetylenic alcohols of the tetrahydrothiopyran series described in this paper are thick liquids or crystals with a slight odor. They form a characteristic precipitate of silver acetylenide with ammoniacal silver nitrate. Their hydrogenation to the corresponding vinyl alcohols in the presence of a Pd catalyst is a violent reaction that evolves heat.

EXPERIMENTAL

The tetrahydro-γ-thiopyrones were synthesized by the action of hydrogen sulfide upon vinyl allyl ketones, as described in a previous report [4]:

2,5-Dimethyl-4-ethynyltetrahydrothiopyran-4-ol (II)

90 ml of absolute ether and 5.4 g of powdered potassium hydroxide were placed in a three-necked flask. Acetylene was passed through the ether at a bath temperature of -8°, until the latter was saturated. Then the acetylene was passed through uninterruptedly and the solution was stirred vigorously for 1.5 hours while a solution of 14 g of 2,5-dimethyltetrahydro-1-thiopyran-4-one (b.p. 71°) in 70 ml of absolute ether was gradually added. The vigorous stirring and the passage of acetylene through the mixture were continued for another 3 hours. The ether solution was poured into alkali and washed with water and a 5% solution of hydrochloric acid until its reaction was neutral. The alkali was dissolved in the water, and the aqueous solution was extracted with ether; the ether extract was washed, and the combined ether solutions were dried with magnesium sulfate. Vaccuum fractionation yielded 3 g of the initial thiopyrone and 5.8 g of 2,5-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (II) as a viscous, colorless liquid:

B.p. 88° at 3 mm; n_D^{20} 1.5250; d_4^{20} 1.0680.

MR found 48.84; calculated 49.05.

7.310 mg substance: 16.984 mg CO_2; 5.242 mg H_2O.

Found %: C 63.41; H 8.02.

$C_9H_{14}OS$. Calculated %: C 63.50; H 8.29.

4.106 mg substance: 2.412 ml 0.02 N iodine solution.

Found %: S 18.83.

$C_9H_{14}OS$. Calculated %: S 18.84.

2,5-Dimethyl-4-ethyltetrahydrothiopyran-4-ol (III)

a) 3.5 g of the 2,5-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (II) described above was dissolved in 30 ml of alcohol and hydrogenated in the presence of 0.2 g of a Pd catalyst deposited on calcium carbonate. 1000 ml of hydrogen (748 mm, 16°) was absorbed as against 1010 ml required theoretically. Vacuum fractionation yielded 3.1 g of 2,5-dimethyl-4-ethyltetrahydrothiopyran-4-ol, a colorless liquid:

B.p. 110-111° at 8 mm; n_D^{20} 1.5140; d_4^{20} 1.0344.

MR found 50.70; calculated 51.06.

3.571 mg substance: 1.999 ml 0.02 N iodine solution
3.959 mg substance: 2.215 ml 0.02 N iodine solution
Found %: S 17.96, 17.93.
$C_9H_{18}OS$. Calculated %: S 18.35.

b) A solution of 14 g of 2,5-dimethyltetrahydro-1-thiopyran-4-one (I) in 50 ml of absolute ether was added in the course of an hour to a Grignard reagent, prepared from 3 g of magnesium, 14 g of ethyl bromide, and 40 ml of absolute ether. Then the reaction mass was boiled for 15 hours with a reflux condenser. The cooled solution was decomposed with 90 ml of 5% hydrochloric acid and then treated in the usual manner.

The yield was 12.6 g of 2,5-dimethyl-4-ethyltetrahydrothiopyran-4-ol (III):

B.p. 99-100° at 5 mm; n_D^{20} 1.5100; d_4^{20} 1.0280.
MR found 50.70; calculated 51.06.
5.750 mg substance: 13.102 mg CO_2; 5.389 mg H_2O.
Found %: C 62.18; H 10.48.
$C_9H_{18}OS$. Calculated %: C 62.03; H 10.41.

2,3,6-Trimethyl-4-ethynyltetrahydrothiopyran-4-ol (V)

11.6 g of powdered potassium hydroxide and 240 ml of absolute ether were placed in a three-necked flask. The solution was saturated with acetylene at -10°. Then the flow of acetylene was continued for 2 hours while 32 g of 2,3,6-trimethyltetrahydro-1-thiopyran-4-one (IV) (b.p. 79° at 8 mm, n_D^{18} 1.4950) was added. After that the flow of acetylene was continued for another 4 hours, the temperature of the bath gradually being raised to room temperature. The product was given the treatment described above, fractionation yielding 18.1 g of 2,3,6-trimethyl-4-ethynyltetrahydrothiopyran-4-ol (V), a viscous, colorless liquid with a slightly moldy odor:

B.p. 102-102.5° at 5 mm; n_D^{20} 1.5185; d_4^{20} 1.0471
MR found 53.45; calculated 53.67.
4.616 mg substance: 2.476 ml 0.02 N iodine solution.
3.240 mg substance: 1.703 ml 0.02 N iodine solution.
Found %: S 17.20, 17.23.
$C_{10}H_{18}OS$. Calculated %: S 17.39.

It forms a characteristic white precipitate of silver acetylenide when reacted with ammoniacal silver nitrate.

2,3,6-Trimethyl-4-vinyltetrahydrothiopyran-4-ol (VI)

14.8 g of the 2,3,6-trimethyl-4-ethynyltetrahydrothiopyran-4-ol (V) described above was hydrogenated in a solution of 80 ml of alcohol in the presence of 0.2 g of a Pd catalyst.

1 molecule of hydrogen (2 liters at 752 mm and 20°) was absorbed in 1.5 hours with the evolution of considerable heat (60-70°), after which hydrogenation was broken off. Vacuum fractionation yielded 14 g of 2,3,6-trimethyl-4-vinyltetrahydrothiopyran-4-ol (VI) as a colorless liquid with a pleasant odor:

B.p. 109.5-110° at 7.5 mm; n_D^{20} 1.5148; d_4^{20} 1.0226.
MR found 54.92; calculated 55.20.
6.470 mg substance: 15.215 mg CO_2; 5.722 mg H_2O.
Found %: C 64.18; H 9.89.
$C_{10}H_{18}OS$. Calculated %: C 64.44; H 9.73.

3.438 mg substance: 1.809 ml 0.02 N iodine solution.
3.410 mg substance: 1.803 ml 0.02 N iodine solution.
Found %: S 16.87, 16.95.
$C_{10}H_{18}OS$. Calculated %: S 17.20.

Treatment with ammoniacal silver nitrate produced no precipitate at all.

2,3,6-Trimethyl-4-ethyltetrahydrothiopyran-4-ol (VII)

a) 4.5 g of 2,3,6-trimethyl-4-ethynyltetrahydrothiopyran-4-ol (V) was dissolved in 35 ml of alcohol and hydrogenated in the presence of 0.1 g of a Pd catalyst.

770 ml of hydrogen was absorbed in 6 hours and another 410 ml in the succeeding 18 hours, or a total of 1180 ml (18°, 748 mm) as against the 1190 ml required by theory, another 0.1 g of Pd catalyst having been added when the experiment was half over.

Vacuum fractionation yielded 3.8 g of 2,3,6-trimethyl-4-ethyltetrahydrothiopyran-4-ol (VII) as a colorless liquid with a moldy odor:

B.p. 109° at 7 mm; n_D^{20} 1.5085; d_4^{20} 1.0147.
MR found 55.31; calculated 55.66.
4.840 mg substance: 11.260 mg CO_2; 4.510 mg H_2O.
4.995 mg substance: 11.662 mg CO_2; 4.660 mg H_2O.
Found %: C 63.49, 63.51; H 10.43, 10.44.
$C_{10}H_{20}OS$. Calculated %: C 63.73; H 10.69.

3.690 mg substance: 1.933 ml 0.02 N iodine solution.
4.190 mg substance: 2.204 ml 0.02 N iodine solution.
Found %: S 16.79, 16.87.
$C_{10}H_{20}OS$. Calculated %: S 17.01.

b) 2,3,6-Trimethyl-4-ethyltetrahydrothiopyran-4-ol was likewise synthesized by the action of ethylmagnesium bromide upon 2,3,6-trimethyltetrahydro-4-thiopyrone; its constants were as follows:

B.p. 106.6-107° at 6 mm; n_D^{20} 1.5083; d_4^{20} 1.0163.
MR found 55.19; calculated 55.66.
4.380 mg substance: 2.376 ml 0.02 N iodine solution.
Found %: S 16.71.
$C_{10}H_{20}OS$. Calculated %: S 17.01.

Dehydration of 2,3,6-Trimethyl-4-vinyltetrahydrothiopyran-4-ol

a) 17.2 g of the vinylthiopyranol (VI) was distilled in a 17-mm vacuum in the presence of 5 g of anhydrous potassium bisulfate. The splitting off of water commenced at a bath temperature of 150-160°. This yielded 3 g of the initial carbinol and 8.8 g of a diene (VIII) as a yellowish liquid:

B.p. 85° at 9 mm; n_D^{20} 1.5278; d_4^{20} 0.9602.
MR found 53.94; calculated 53.21.
5.040 mg substance: 2.964 ml 0.02 N iodine solution.
3.380 mg substance: 2.010 ml 0.02 N iodine solution.
Found %: S 18.85, 19.06.
$C_{10}H_{16}S$. Calculated %: S 19.06.

b) 11.2 g of 2,3,6-trimethyl-4-vinyltetrahydrothiopyran-4-ol was distilled in vacuum in the presence of 0.35 g of p-toluenesulfonic acid and pyrogallol. Water began to be split off vigorously at a bath temperature of 160-170°. This yielded 6.5 g of the diene (VIII) already described, with a b.p. of 95-100° at 14 mm, n_D^{18} 1.5260.

Condensation of the Diene (VIII) with Maleic Anhydride

1.6 g of the diene (VIII) and 1 g of maleic anhydride were dissolved in 3 ml of benzene. The anhydride dissolved upon slight heating, the product turning yellow. The solution was heated in a sealed ampoule for 1 hour at a bath temperature of about 100°. Then the ampoule was opened, the polymerized product, amounting to some 0.1 g, was isolated, and the solvent driven off. Treatment of the residue with methanol yielded about 0.4 g of the monomethyl ester of the condensation product (IX) as small needles with a m.p. of 157° (from a mixture of petroleum ether and benzene).

2.977 mg substance: 0.942 ml 0.02 N iodine solution.
3.100 mg substance: 0.971 ml 0.02 N iodine solution.
Found %: S 10.37, 10.28.
$C_{15}H_{22}O_4S$. Calculated %: S 10.67.
0.0700 g substance: 2.35 ml 0.1 N KOH solution.
Found: M 298; calculated 300.4.

2,3,6-Trimethyl-4-ethyltetrahydrothiopyran (X)

3.2 g of the diene (VIII) was dissolved in 30 ml of alcohol and hydrogenated in the presence of 0.1 g of Pd catalyst. About 300 ml of hydrogen was absorbed in the first 6 hours. Then another 470 ml of hydrogen was absorbed during 32 hours after 0.2 g of Pd catalyst had been added. The alcohol was driven off, and the substance was distilled in vacuum. This yielded 2.5 g of a substance with a b.p. of 73-74° at 6 mm; n_D^{20} 1.4980.

The constants of the substance did not change after another endeavor to dehydrate it with a Pd catalyst.

The synthesized 2,3,6-trimethyl-4-ethyltetrahydrothiopyran is a liquid:

B.p. 75-76°; n_D^{20} 1.4970; d_4^{20} 0.9355.
MR found 53.91; calculated 54.15.
5.240 mg substance: 13.375 mg CO_2; 4.990 mg H_2O.
6.280 mg substance: 16.027 mg CO_2; 5.974 mg H_2O.
Found %: C 69.66, 69.64; H 10.65, 10.64.
$C_{10}H_{20}O8$. Calculated %: C 69.68; H 11.68.

To judge by the analysis, the substance was not entirely pure and apparently contained a certain amount of products of incomplete hydrogenation.

2-Methyl-4-ethynylhexahydrothiochroman-4-ol (XII)

16.8 g of powdered potassium hydroxide and 400 ml of absolute ether were placed in a three-necked flask. The solution was saturated with acetylene at -8°. Then the acetylene was passed through the solution for three hours with uninterrupted stirring while 53 g of trans-thiochromanone (XI) (m.p. 78°) dissolved in 200 ml of absolute ether was added. After the ketone had been added, the acetylene was passed through the solution for another 4 hours, the bath temperature being gradually raised to room temperature. The product was given the usual treatment that very same day.

Vacuum fractionation yielded 40.7 g of a mixture of isomeric 2-methyl-4-ethynylhexahydrothiochroman-4-ols (XII); b.p. 145-147° at 8 mm; n_D^{20} 1.5400. Residue 11 g.

Treatment of the mixture of isomeric thiochromanols (XII) with alcohol yielded 13 g of a high-melting isomer with a m.p. of 112° (from alcohol).

8.57 mg substance: 21.58 mg CO_2; 6.58 mg H_2O.
Found %: C 68.70; H 8.59.
$C_{12}H_{18}OS$. Calculated %: C 68.53; H 8.60.
3.142 mg substance: 1.495 ml 0.02 N iodine solution.
Found %: S 15.26.
$C_{12}H_{18}OS$. Calculated %: S 15.21.

Treatment of the residual mixture with ligroin (b.p. 105-120°) yielded 10.5 g of low-melting isomer (XII) with a m.p. of 69° (from ligroin and petroleum ether).

13.81 mg substance: 34.71 mg CO_2; 10.34 mg H_2O.
8.07 mg substance: 20.34 mg CO_2; 6.28 mg H_2O.
Found %: C 68.59, 68.78; H 8.49, 8.69.
$C_{12}H_{18}OS$. Calculated %: C 68.53; H 8.60.

Isolation of the low-melting isomer left an oil that represented a mixture of both isomers. Both isomeric acetylenic alcohols (XII) form a characteristic white precipitate of silver acetylenides when treated with ammoniacal silver nitrate. When heated to 120-130° with powdered alkalis, the acetylenic alcohols (XII) decompose, liberating acetylene.

The acetylenic glycol (XIX) with a m.p. of 221° (from alcohol) was isolated from the residue by treatment with alcohol after the thiochromanone (XII) had been driven off.

0.1264 g substance; 20 g of dioxane: Δt 0.800°.
Found: M 363.4.
$C_{22}H_{34}O_2S_2$. Calculated: M 394.6.

8.92 mg substance: 21.93 mg CO_2; 6.76 mg H_2O.
9.73 mg substance: 23.79 mg CO_2; 7.65 mg H_2O.
Found %: C 67.05, 66.72; H 8.49, 8.79.
$C_{22}H_{34}O_2S_2$. Calculated %: C 66.95; H 8.66.

The glycol exhibits a negative reaction for acetylenic hydrogen when tested with ammoniacal silver nitrate. When heated to 120-130° with a powdered alkali (10% by weight of the glycol), the glycol decomposes, liberating acetylene.

2-Methyl-4-vinylhexahydrothiochroman-4-ol (XIII)

a) High-melting isomer. 10 g of the high-melting acetylenic alcohol (XII) (m.p. 112°) was hydrogenated in 40 ml of a mixture of alcohol and ether in the presence of a Pd catalyst. One molecule of hydrogen (1.2 liters at 26° and 738 mm) was absorbed in 2 hours, after which hydrogenation was stopped. The product crystallized after the solvent had been driven off. This yielded 9.5 g of the high-melting 2-methyl-4-vinylhexahydrothiochroman-4-ol (XIII) with a m.p. of 94° (from alcohol).

3.340 mg substance: 8.285 mg CO_2; 2.855 mg H_2O.
Found %: C 67.70; H 9.56.
$C_{12}H_{20}OS$. Calculated %: C 67.88; H 9.49.

b) Low-melting isomer. 4.5 g of the low-melting acetylenic alcohol (XII) (m.p. 69°) was hydrogenated in the presence of a Pd catalyst in a solution of 25 ml of alcohol. One molecule of hydrogen (540 ml at 26° and 740 mm) was absorbed in 20 minutes, after which hydrogenation was stopped. The alcohol was driven off and the product distilled in vacuum. This yielded 3.8 g of a substance with a b.p. of 155-156° at 11 mm, which crystallized in the receiver. The low-melting isomer of 2-methyl-4-vinylhexahydrothiochroman-4-ol (XIII) fuses at 76° (from ligroin).

11.16 mg substance: 27.88 mg CO_2; 9.45 mg H_2O.
9.60 mg substance: 23.89 mg CO_2; 8.13 mg H_2O.
Found %: C 68.18, 67.92; H 9.50, 9.47.
$C_{12}H_{20}OS$. Calculated %: C 67.88; H 9.49.

Neither isomer of the vinylic alcohol (XIII) forms a precipitate with ammoniacal silver nitrate.

2-Methyl-4-ethylhexahydrothiochroman-4-ol (XIV)

a) Solid isomer. 1 g of the high-melting acetylenic alcohol (XII) (m.p. 112°) was hydrogenated in the presence of 0.1 g of a Pd catalyst deposited on calcium carbonate. Two molecules of hydrogen (240 ml at 27° and 744 mm) were absorbed in 2 hours, and hydrogenation was stopped. Vacuum fractionation yielded 0.85 g of a substance with a b.p. of 148° at 13 mm, which crystallized in the receiver. This 2-methyl-4-ethylhexahydrothiochroman-4-ol (XIV) consists of crystals with a m.p. of 55° (from petroleum ether).

11.98 mg substance: 29.51 mg CO_2; 11.03 mg H_2O.
Found %: C 67.23; H 10.30.
$C_{12}H_{22}OS$. Calculated %: C 67.21; H 10.31.

b) Liquid isomer. 1.2 g of the low-melting acetylenic alcohol (XII) (m.p. 69°) was dissolved in 13 ml of alcohol and hydrogenated in the presence of 0.1 g of a Pd catalyst. Two molecules of hydrogen (265 ml at 25° and 742 mm) were absorbed in 8 hours, after which hydrogenation was stopped. Vacuum fractionation yielded 0.75 g of an ethylthiochromanol (XIV) as a viscous, colorless liquid, b.p. 154° at 9 mm, n_D^{20} 1.5294, which did not crystallize even upon long standing and chilling to -10°.

Action of Ethylmagnesium Bromide upon 2-Methylhexahydro-1-thiochroman-4-one

A solution of 10 g of the trans-thiochromanone (XI) (m.p. 78°) in 60 ml of absolute ether was gradually added in the course of 1 hour to a Grignard reagent, prepared from 1.7 g of magnesium and 7.8 g of ethyl bromide in 30 ml of ether. The reaction mass was then boiled for 15 hours. 70 ml of 5% hydrochloric acid was added drop by drop to the chilled solution, after which the product was treated in the usual manner. Fractionation yielded 9 g of a substance, b.p. 148-154° at 11 mm, which crystallized in the receiver. Recrystallization yielded the ethylthiochromanol (XIV) with a m.p. of 55° (from petroleum ether), which exhibited no depression when mixed with the preceding sample. The liquid fraction of 3 g, obtained after the crystals had been separated, contains, in the main the same crystalline ethylthiochromanol (XIV), as was proved by oxidizing it to a sulfone with a m.p. of 146° (vide infra).

Sulfones of 2-Methyl-4-ethylhexahydrothiochroman-4-ol

a) 1 g of the crystalline isomer of the ethylthiochromanol (XIV) (m.p. 55°) was dissolved in 8 ml of acetone. 3 5 ml of 10% sulfuric acid was added to the solution, after which 1 g of potassium permanganate was gradually added with stirring and chilling with ice water. The manganese dioxide was filtered out and washed with hot water. The filtrate and the wash waters were combined. This yielded 1 g of the sulfone (XV), m.p. 146° (from a mixture of benzene and ligroin).

4.245 mg substance: 9.075 mg CO_2; 3.307 mg H_2O.
Found %: C 58.34; H 8.71.
$C_{12}H_{22}O_3S$. Calculated %: C 58.50; H 8.98.

b) 0.75 g of the liquid isomer of the ethylthiochromanol (XIV) was dissolved in 6 ml of acetone, and 3 ml of 10% sulfuric acid was added to the solution. 0.8 g of potassium permanganate was then added with stirring and chilling with ice water.

The reaction product was given the usual treatment. This yielded a sulfone with a m.p. of 176° (from benzene).

12.12 mg substance: 26.11 mg CO_2; 9.80 mg H_2O.
Found %: C 58.70; H 9.04.
$C_{12}H_{22}O_3S$. Calculated %: C 58.50; H 8.98.

Dehydration of 2-Methyl-4-vinylhexahydrothiochroman-4-ol

a) 9.5 g of the high-melting vinylthiochromanol (XIII) (m.p. 94°) was distilled in vacuum in the presence of 0.3 g of p-toluenesulfonic acid and pyrogallol. Water began to be split off at a bath temperature of 140°. Distillation was continued at 15 mm and a bath temperature of 179-210°. This yielded 4.1 g of a diene (XVI), a greenish-yellow liquid with a singular odor:

B.p. 140-141° at 12 mm; n_D^{20} 1.5507; d_4^{20} 1.0012.
MR found 61.25; calculated 60.25.
9.39 mg substance: 25.45 mg CO_2; 7.92 mg H_2O.
14.49 mg substance: 39.27 mg CO_2; 12.26 mg H_2O.
Found %: C 73.97, 73.96; H 9.41, 9.46.
$C_{12}H_{18}S$. Calculated %: C 74.17; H 9.34.

b) 8.5 g of the low-melting vinylthiochromanol (XIII) (m.p. 76°) was distilled in vacuum in the presence of 0.2 g of p-toluenesulfonic acid and pyrogallol. Water began to be split off at 140°. This yielded 4.3 g of a diene (XVI) with a b.p. of 138-141° at 13 mm; n_D^{20} 1.5465. The bath temperature did not exceed 180° during distillation.

Condensation of the Diene (XVI)

a) 2 g of the diene (XVI) synthesized from the high-melting vinylthiochromanol (XIII) and 1.1 g of maleic anhydride were dissolved in 3 ml of benzene with slight heating. Crystals were formed on the walls. The crystals were filtered out 48 hours later, This yielded 0.8 g of a condensation product (XVII) with a m.p. of 154° (from a mixture of benzene and petroleum ether).

b) Condensation of 0.55 g of maleic anhydride with 1 g of the diene (XVI) synthesized from the low-melting vinylthiochromanol (XIII) yielded 0.2 g of a product (XVII) with a m.p. of 154°, which exhibited no depression when mixed with the preceding sample.

4.690 mg substance: 11.330 mg CO_2; 2.835 mg H_2O.
4.930 mg substance: 11.909 mg CO_2; 2.930 mg H_2O.
Found %: C 65.92, 65.93; H 6.73, 6.65.
$C_{16}H_{20}O_3S$. Calculated %: C 65.74; H 6.89.

Saponification of the Anhydride (XVII)

0.2 g of the anhydride (XVII) was boiled for 4 hours with 2 ml of water. After the mixture had cooled, crystals with a m.p. of 206° settled out; they constituted an acid (XVIII) containing two molecules of water of crystallization.

0.0425 g substance: 2.71 ml 0.7 N KOH solution
Found: M 313.2; calculated 346.34.
5.115 mg substance: 10.475 mg CO_2; 3.455 mg H_2O.
4.815 mg substance: 9.845 mg CO_2; 3.330 mg H_2O.
Found %: C 55.89, 55.80; H 7.56, 7.74.
$C_{16}H_{22}O_4S \cdot 2H_2O$. Calculated %: C 55.48; H 7.56.

SUMMARY

1. Tetrahydro-γ-thiopyranones enter into condensation reactions with acetylene under the influence of powdered potassium hydroxide, forming the corresponding tetrahydro-γ-thiopyranols of the acetylene series, with yields of 50-70%.

2. The acetylenic tetrahydro-γ-thiopyranols are selectively hydrogenated by a Pd catalyst, first forming vinyl, and later saturated (ethyl) tetrahydro-γ-thiopyranols.

3. Two geometrical isomers of the trans series of 2-methyl-4-ethynylhexahydrothiochroman-4-ol (XII) were isolated; their hydrogenation yielded the corresponding isomeric vinyl and saturated thiochromanols (XIII) and (XIV).

4. The corresponding sulfones (XV) were synthesized by oxidizing the isomeric ethylthiochromanols.

5. Splitting water off from the vinyltetrahydro-γ-thiopyranols yielded the dienes (VIII) and (XVI), which condense with maleic anhydride to form the corresponding products (IX) and (XVII).

6. Condensing acetylene with 2-methylhexahydro-1-thiochroman-4-one yielded an acetylenic glycol (XIX).

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* See CB translation p. a211 and ff.

** See previous article. p. a837

COMPOUNDS OF BORON FLUORIDE AS NEW ALKYLATION AND POLYMERIZATION CATALYSTS

V. ALKYLATION OF ISOPENTANE BY PROPYLENE

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The first catalytic alkylations of the isoparaffins by olefins, largely in accordance with the following equation:

$$\text{iso-}C_nH_{2n+2} + C_mH_{2m} \longrightarrow \text{iso-}C_pH_{2p+2},$$

where $p = n + m$, were effected in 1935 with the aid of boron fluoride compounds [1]: BF_3 with H_2O and BF_3 with HF. In the former case the hydrate of boron fluoride, $H_2O \cdot BF_3$, that was formed was the catalyst, whereas in the latter the fluoboric acid HBF_4 was evidently the catalyst.

After 1939, the catalytic alkylation reaction was employed industrially in the synthesis of iso-octane and di-isopropyl and dimethylpentanes - the high octane componenets of avaiation gasoline. In industry the first catalyst employed was sulfuric acid [2], hydrofluoric acid being employed later on [3], and recently aluminum chloride being used to synthesize di-isopropyl [4]. Almost nothing has been published as yet on the industrial application of boron fluoride in alkylation reactions, although increasing attention is being devoted to catalysts of this type of late. Several patents were issued during 1942-1947 for catalysts for the alkylation of isoparaffins by olefins (ethylene, propylene, and the butylenes) using solutions of boron fluoride in water. The general formula of the catalyst is:

$$BF_3 \cdot nH_2O,$$

where $n = 1 - 1.5$. These compounds are prepared by passing BF_3 through water directly [5].

Aqueous solutions of hydrofluoric acid saturated with boron fluoride [6], constituting a ternary system $HF + H_2O + BF_3$, have been proposed for alkylating isoparaffins by olefins. In 1947 a detailed study was published [7], in which the foregoing system was employed to effect the alkylation of isobutane with ethylene in a pilot plant, with satisfactory results.

Compounds of boron fluoride with inorganic acids are very active alkylation catalysts. Thus, in 1934 and 1935 patents were applied for, covering catalysts for condensation reactions, produced by saturating acids containing pentavalent phosphorus (H_3PO_4 and its mixtures with $H_4P_2O_7$) with boron fluoride [8]. But no claims were filed for these catalysts in alkylation reactions.

Beginning in 1942, however, a number of patents were issued covering catalysts for alkylating isoparaffins with olefins, using solutions of BF_3 in H_3PO_4. In one of the recent patents [10] issued in 1946 it is stated that the catalyst in the system is a molecular compound of BF_3 and H_3PO_4, with the general formula $H_3PO_4 \cdot BF_3$. It should be noted that the authors of the present paper prepared this compound and studied its physical and chemical properties as long ago as 1945 [11].

In the present paper the alkylation of isopentane by propylene with various types of boron-fluoride compounds is systematically studied for the first time.

Isopentane is a convenient isoparaffin hydrocarbon for use in studying the alkylation reaction under laboratory conditions, as it is a liquid, and the reaction can be effected at atmospheric pressure; isopentane is somehat harder to alkylate than isobutane, but this is not a serious hindrance.

EXPERIMENTAL

Chemically pure isopentane, with a b.p. of 27.8°, d_4^{20} 0.6197 and n_D^{20} 1.3539, was used in our experiments. The propylene was prepared by dehydrating isopropyl alcohol, with a b.p. of 83°, over alumina at 380°.

The compounds of boron fluoride with acids, water, ethers, and alcohols were prepared by passing BF_3 through the corresponding substance; the amount of boron fluoride absorbed corresponded to the chemical composition of the substances, as listed in Table 1. All of them were hygroscopic liquids that fumed when exposed to the air. The boron fluoride was prepared from calcium fluoride, boron oxide, and sulfuric acid.

Alkylation was carried out in the apparatus described below.

Propylene from the gas tank passed through the rheometer at a rate of 2 liters/hour; from the rheometer it flowed through a calcium-chloride tower for scrubbing and then to the reactor. The unabsorbed gas was passed through a cooler and safety tower and was then collected in a gas tank. Within the reactor the stirring together of the isopentane, the liquid catalyst, and the olefin that passed through was effected by a high-speed rotating frame stirrer with a seal, the sealing fluid being a mercury-oil emulsion. In every run the reactor was filled with 20 ml of catalyst and 50 ml of isopentane, and 4.5 liters of propylene was passed through, which corresponded to a 1:2.3 molar ratio of the olefin to the isoparaffin.

After the run, the hydrocarbon layer was separated from the catalyst (which was insoluble in hydrocarbons), washed with an alkaline solution and then with water, dried with calcium chloride, and fractionated in a rectifying tower. Products taken from parallel runs were used in fractionation. The yield of the alkylate was evaluated by the volume of the hydrocarbons that boiled away at over 50°.

To get an idea of the activity of a number of catalysts, we tried out various boron-fluoride compounds, sulfuric acid, and aluminum chloride in the alkylation of isopentane with propylene under comparable experimental conditions.

As the experimental data indicate (Table 1), the compounds of boron fluoride with compounds containing hydroxyl, which measurements of conductivity proved to be strong acids, are catalytically active in alkylation reactions. Compounds of boron fluoride with ethers and esters, as well as with pyridine and amines, are inactive in alkylating the isoparaffins.

Of the boron-fluoride compounds tested, the best catalysts for the alkylation of the isoparaffins proved to be $P_2O_5 + nH_2O + BF_3$ and $H_2O \cdot BF_3$. Their action is similar to that of sulfuric and hydrofluoric acids insofar as the general reaction pattern is concerned.

The effect of temperature upon the alkylation reaction when the $0.5P_2O_5 + BF_3 + H_2O$ catalyst is used is shown below (Table 2).

The optimum region is the temperature range of 0° to +20°, as indicated by the yield, the bromine number, and the specific gravity of the alkylate.

The effect of the amount of catalyst employed in proportion to the hydrocarbon mixture is indicated in the following series of tests (Table 3).

TABLE 1

Activity of Various Compounds of Boron-Fluoride Compounds as Catalysts in the Alkylation of Isopentane by Propylene

Exp. No.	Catalyst	Yield of hydrocarbons boiling above 50°			Specific gravity of alkylate d_4^{20}	Service life of catalyst
		ml	% of theory	% of propylene employed		
1	$0.5P_2O_5 + 1.5H_2O + BF_3$	18.4	73.6	175	0.713	can be used repeatedly
2	$0.5P_2O_5 + BF_3 + H_2O$ . .	18.6	71.5	170	0.7100	
3	$H_2O \cdot BF_3$	18.5	70.5	168	0.707	
4	$BF_3 \cdot 2.5H_2SO_4$	18.1	69	164	0.7050	Activity drops after first run
5	$CH_3OH \cdot BF_3$	11	43	105	0.7538	
6	$C_2H_5OH \cdot BF_3$	9	38	90	0.771	
7	$HPO_3 \cdot BF_3$	6	23	55	0.730	Catalyst practically inactive
8	$CH_3COOH \cdot BF_3$	5	19	45	0.69	
9	$C_5H_5N \cdot BF_3$	–	0	0	–	
10	$C_6H_5OH \cdot BF_3$	–	0	0	–	The phenol is alkylated
11	$(C_2H_5)_2O \cdot BF_3$	–	0	0	–	
12	$CH_3COOC_2H_5 \cdot BF_3$	–	0	0	–	
13	$(CH_3C_6H_4O)_3PO \cdot BF_3$ . . .	–	0	0	–	
14	BF_3	–	0	0	–	Literature data
15	$AlCl_3$	9.6	40	95	0.7592	Activity drops rather rapidly
16	H_2SO_4 (101%)	16.6	70	165	0.7076	can be used once

The effect of temperature upon the alkylation reaction when the 0.5 P_2O_5 + BF_3 + H_2O catalyst is used is shown below (Table 2).

Table 2

Temperature °C	d_4^{20}	Bromine number	Alkylate yield (in % of propylene)
– 10	0.7392	6	120
– 5	0.7291	3	156
± 0	0.7111	1	181
+ 20	0.709	0-0.3	180

TABLE 3

Ratio of catalyst to hydrocarbon mixture	Alkylate yield in % of propylene
1:13	125
1:6.5	180
1:3.25	179
1:2.16	182

TABLE 4

No. of tests	Alkylate yield, g	d_4^{20}	Alkylate yield, % of propylene
1	18.1	0.7109	206
2	18	0.7075	205
3	16.4	0.7231	164
4	11.2	0.7575	128

The test results show that the reaction mixture should contain at least 15-20% of catalyst for a fairly efficient reaction.

As for the effect of the propylene-isopentane ratio, it is a matter of common knowledge that the yield and quality of an alkylate are improved by increasing the excess of the isoparaffin, as this suppresses the secondary alkylation

and polymerization reactions. This likewise holds true for the reaction discussed here, and there is no need, therefore, to cite details; we may confine ourselves to stating that a C_3H_6:iso-C_5H_{12} ratio of from 1:4 to 1:6 is satisfactory.

As operations proceed, the activity of the three best catalysts cited above drops off owing to the absorption of unsaturated compounds, resulting in dilution; this drop is considerably smaller, however, than in the case of sulfuric acid, which we were unable to use more than once in our test conditions. Table 4 shows the useful life of boron fluoride hydrate, $H_2O \cdot BF_3$, in the alkylation reaction.

The operating stability of several of the catalysts tested is shown in the curves below (Fig. 1).

To determine the fractional, and later the chemical, composition, the washed and dried reaction products were run through a rectifying tower, equivalent in fractionating ability to 34 theoretical trays. The fractional composition is shown in detail in Table 5.

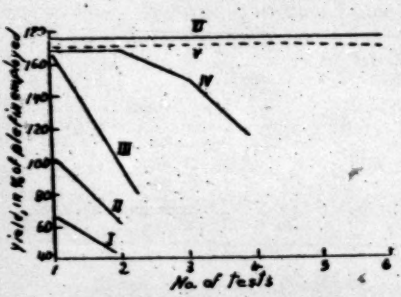

Fig. 1. Service life of catalysts used in alkylating isopentane with propylene.

I - $BF_3 \cdot HPO_3$; II - BF_3 + CH_3OH; III-$BF_3 \cdot 2H_2SO_4$; IV-$BF_3 \cdot Et_2O$; V-$0.5P_2O_5 + H_2O + BF_3$; VI-$0.5P_2O_5 + 1.5H_2O + BF_3$

With all three catalysts, the high boiling residue (above 170°) consists of a mixture of isoparaffins, as is indicated by the low bromine number of 1-2, the specific gravity, the determination of the molecular weight cryoscopically, and the refraction. It is worthy of note that when sulfuric acid is used for alkylation, olefins accumulate in the residue, as is indicated by the bromine number of 10 - 15.

Curves of the fractionation of the alkylation products are shown below for the four tests using different catalysts.

TABLE 5

Fractional Composition of Alkylates in the Alkylation of Isopentane by Propylene (Catalyst = $H_2O \cdot BF_3$)

Test No.	Boiling range, °	Volume of fraction, ml	Fractional composition, % by volume	d_4^{20}	n_D^{20}	Remarks
1	40-50°	1	–	0.620	–	Pentanes
2	50-60	0.2	0.5	0.6674	1.3785	
3	60-90	1.8	4.4	–	–	
4	90-110	9.4	22.8	0.6888	1.3915	47.3% iso-octanes
5	110-120	10	24.4	0.7084	1.3975	
6	120-130	0.7	1.7	0.7100	1.3086	
7	130-140	0.5	1.2	–	–	
8	140-150	1.6	4	0.7171	1.4028	
9	150-160	1	2.2	0.7246	1.4086	
10	160-170	3.4	8.8	0.7338	1.4136	69.5% distils over up to 170°
11	170	11.8	28.7			

TABLE 6

Fractional Composition of Heavy Residue of Alkylate with $0.5P_2O_5$ + $1.5H_2O$ + BF_3 as Catalyst

Boiling range, °	Volume of fraction, ml	Volume of fraction, %	d_4^{20}	n_D^{20}	Molecular weight	Remarks
170-190°	0.5	1.7	0.7673	1.4307		
190-210	1.9	6.5	–	–	152	Bromine No. 1.9
210-230	4.6	16	0.7378	1.4372	189	
230-250	5.4	18.6	0.789	1.4439	197	
250-270	2.8	9.6	0.7964	1.4469	240	
270-300	7.4	25.5	0.8053	1.4516	262	
300-350	4	13				
loss	2.4					

TABLE 7

Chemical Composition of Octane Fractions of Alkylates of Isopentane with Propylene, Using Various Catalysts

H_2SO_4 (principal products) [13]	$0.5P_2O_5 + H_2O + BF_3$	$H_2O \cdot BF_3$
2,3-Dimethylhexane	2,3-Dimethylhexane - 54%	2,5-Dimethylhexane - 55%
2,4-Dimethylhexane	2,4-Dimethylhexane - 14%	2,4-Dimethylhexane - 30%
2,5-Dimethylhexane	2,5-Dimethylhexane - 19%	Other hydrocarbons - 15%
	2,2,3-Trimethylpentane - 6%	
	Other hydrocarbons - 7%	

As may be seen from the figures on fractional composition, high-boiling alkylation products are obtained with the $0.5P_2O_5 + 1.5H_2O + BF_3$ catalyst (Table 6), only about 20% of gasoline distilling over up to 170°, owing to polyalkylation reactions caused by the extremely high activity of the catalyst. The reaction product has a bromine number of 0 - 1, i.e., it contains no unsaturated compounds. The $H_2O \cdot BF_3$ and $0.5P_2O_5 + H_2O + BF_3$ catalysts yield alkylation products whose fractional composition resembles that obtained in sulfuric-acid alkylation, with 50 to 60% of iso-octanes.

After fractionation, the various ten-degree fractions were analyzed spectroscopically by the method of combined light scattering [11] to determine their chemical composition. The analysis data indicated that in all instances the samples contained

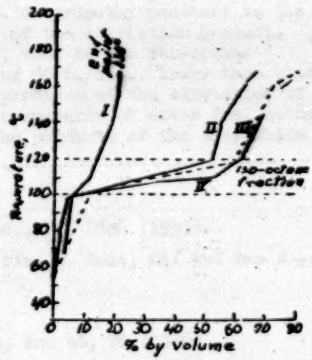

Fig. 2. Fractional composition of alkylation products of isopentane with propylene using various catalysts.

I- $0.5P_2O_5$ + $1.5H_2O$ + BF; II- $BF_3 \cdot H_2O$; III- H_2SO_4; IV- $0.5P_2O_5 + H_2O + BF_3$

no olefins, or aromatic and naphthene hydrocarbons, but were mixtures of iso-paraffin hydrocarbons. The analysis results are given in Table 7.

It is worthy of note that most of the alkylation products consist of little-branched hydrocarbons - dimethylhexanes, and hence the motor-fuel qualities of the alkyl gasoline obtained by the alkylation of isopentane with propylene are not very high. Thus, determination of the octane number of the whole alkylate boiling at more than 30° (after the isopentane had been driven off) by the Motor method, using a Waukesha motor, gave the value of 70.3, that of the iso-octane fraction distilling within the 98-120° range being 80.6. If it is borne in mind that the initial isopentane has an octane number of 89, ie.e, higher than that of its alkylate, and itself is part of the motor fuel, the alkylation of isopentane can hardly be of any practical value for the synthesis of motor-fuel components.

SUMMARY

1. Various types of compounds of boron fluoride have been investigated for the first time as catalysts for the alkylation of isopentane with propylene the yields being determined and the fractional and chemical composition of the alkylates being investigated by the method of combined light scattering.

2. The only compounds of boron fluoride that are catalytically active in the alkylation of isoparaffins are those with substances containing hydroxyl: water, acids, and alcohols. In combination with boron fluoride all these substances behave like strong acids, and their catalytic action is that of the usual acid catalysis. Compounds of BF_3 with ethers, esters, and amino compounds, as well as pure boron fluoride, are catalytically inactive in the alkylation of the isoparaffins.

3. When isopentane is alkylated with propylene in the presence of compounds of boron fluoride with water and phosphoric acids, an alkylation product is formed with a yield of 175-200% of the propylene employed or 70-85% of the theoretical, with a specific gravity under optimum conditions of d_4^{20} 0.705-0.715, with 70-80% by volume distilling up to 170°.

4. The chemical composition of the alkylation products is only slightly dependent upon the catalysts used, as far as the kind of hydrocarbons synthesized is concerned. The iso-octane fraction chiefly consists of dimethylhexanes, hydrocarbons that are but slightly branched: 2,3-, 2,4-, and 2,5-dimethylhexanes, whereas the alkylation of isobutane with butylene yields trimethylpentanes in the iso-octane fraction. As a result, the octane number of the alkylation product, measured by the Motor method, is not very high: 70.3, that of the iso-octane fraction of the alkylation product (b.p. 98-120°) being 80.6, i.e., lower than that of the initial isopentane, which is 89. Hence, the products of the alkylation of isopentane, with propylene cannot be recommended as components of motor fuel owing to their low octane number, as compared to that of the products of the alkylation of isobutane with olefins.

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COMPOUNDS OF BORON FLUORIDE AS NEW ALKYLATION AND POLYMERIZATION CATALYSTS

VI. ALKYLATION OF ISOPENTANE BY ETHYLENE AND ISOBUTYLENE

Y. M. Paushkin and A. V. Topchiev

The catalytic alkylation of isobutane and isopentane by ethylene, discovered in 1935 [1], may be represented by one of the following basic equations:

$$iso\text{-}C_4H_{10} + C_2H_4 \longrightarrow iso\text{-}C_6H_{14}$$

The addition of isobutane to ethylene results principally in the formation of dimethylbutanes, which are employed as high-octane components of motor fuel. This synthesis was first effectuated in 1935 by means of catalysts that were rather inaccessible at the time (BF_3 with H_2O and BF_3 with HF) and therefore did not proceed beyond the laboratory experiments.

One year later the noncatalytic addition of isobutane to ethylene [2] at the high temperature of 500° and the high pressure of 300 atmospheres was discovered [2]. This process was applied industrially, but it did not find wide application because of the complexity and cost of the apparatus required.

A process has been recently developed for the thermo-catalytic alkylation [3] of isobutane by ethylene in the presence of 1 - 2% of organic chlorides, which act catalytically, the reaction therefore taking place at a lower temperature, 300 to 400°, and at a pressure of 200 atm.

Lately, boron fluoride has become easily available and has found practical application in some countries as a catalyst in the organic synthesis industry [4], and this has resulted in ever-increasing attention being focussed on compounds of boron fluoride as alkylation catalysts. Beginning in 1942, a number of patents have been issued [5] for catalysts for alkylating the isoparaffins by olefins, chiefly by ethylene with the aid of solutions of BF_3 in H_3PO_4. In one of the latest patents, issued in 1946 [6], a catalyst for alkylating isobutane with ethylene is proposed, by means of which an alkylate is produced that contains up to 80% of hexanes, some 95% of them being 2,3-dimethylbutane. The catalyst is a molecular compound of boron fluoride and phosphoric acid, with the chemical formula $H_3PO_4 \cdot BF_3$. In none of the similar previous patents was the formula of the catalyst given.

It should be noted that the authors of the present paper [7] produced this compound in 1945, determining its composition and making a detailed study of its physical and chemical properties.

Then several patents were issued for catalysts for alkylating isoparaffins by ethylene and other olefins by means of hydrates of boron fluoride. Thus, in 1942 a patent was issued [8] for alkylating isoparaffins with olefins by means of the $H_2O - BF_3$ system. In other 1944 patents [9], a liquid compound with the general formula of $BF_3 \cdot nH_2O$ is proposed as a catalyst, where $n = 1 - 1.5$; at $n = 1$, this corresponds to a composition of $BF_3 = 79\%$ and $H_2O = 21\%$ and has the chemical formula of a monohydrate of boron fluoride, $H_2O \cdot BF_3$.

The ternary system [10] HF + H_2O + BF_3 and anhydrous hydrofluoric acid with

boron fluoride [11] have been proposed as catalysts for ethylene alkylation. In 1947 a detailed research study [12] was published on the alkylation of isobutane with ethylene by means of the HF – H_2O – BF_3 system, effected in the laboratory and in a pilot plant. The catalyst was prepared by saturating 50% aqueous HF with boron fluoride; it corresponds to the formula $HF \cdot BF_3 \cdot H_2O$ and, apparently, is a chemical compound, since the addition of anhydrous HF to $H_2O \cdot BF_3$ is accompanied by a considerable exothermic effect. The most active catalyst is one consisting of equimolecular quantities of water, hydrogen fluoride, and boron fluoride; its specific gravity is 1.75; the activity of this catalyst is higher than that of boron fluoride hydrate, $H_2O \cdot BF_3$.

A fairly large quantity of raw material has been processed in the pilot plant: some 200 kg of isobutane and 38 kg of ethylene were passed through the reactor, 25% of whose volume is filled with the liquid catalyst. It was found during operation that the catalyst can yield 8 to 10 volumes of alkylate per volume of catalyst (consumption about 25%); but if the catalyst is continually activated with BF_3 and periodically activated with HF, its consumption drops to 1.5-2.5%.

During alkylation, the isobutane-ethylene ratio used was 2 to 3.5, the duration of contact between the reagents being 15 to 30 minutes with intensive stirring and a pressure of 16 atmospheres. Under these conditions the yield of alkylate reached 200,250%, based on the ethylene used, the alkylate containing 60 to 70% of 2,3-dimethylbutane.

2,3-Dimethylbutane, called di-isopropyl, was first produced industrially in 1944 [13]. Alkylation of isobutane by ethylene was effected with a liquid catalytic coordination compound of $AlCl_3$ with a hydrocarbon at a pressure of 21 atm in the presence of 0.05-0.3% of HCl with a C_2H_4 – iso-C_4H_{10} molar ratio of 1:3.9-5.5. Under these conditions, 75-85% of the ethylene went to form di-isopropyl, the yield of alkylate being 270-280%, based on the ethylene employed. 58-67% of the alkylate consisted of 2,3-dimethylbutane; the consumption of the catalyst – aluminum chloride – was of the order of 1 kg per 110 liters of alkylate produced.

The alkylation of isopentane by isobutylene has not been touched on in the literature, since isopentane itself is a valuable constituent of motor fuel, whereas the isononanes synthesized in the reaction are less valuable than isopentane or the iso-octanes, though the alkylation of isobutane by the pentanes has been employed in practice. Alkylates of this type consist of 40-55% of isononanes and 30-40% of iso-octanes. The process of alkylating isobutane with butenes and pentenes has been developed by Mamedaliev in the USSR [14].

The present paper investigates the alkylation of isopentane by ethylene and isobutylene; though this cannot yield high-octane alkylates, it is of interest in evaluating the activity of various catalysts.

EXPERIMENTAL

The isopentane used in the reaction was first rectified in a tower that was equivalent to 12 theoretical trays in its fractionating ability: the fraction boiling at 27.8-28°, whose boiling point corresponds to that of isopentane (27.8°) was collected. The ethylene and isobutylene were prepared by dehydrating ethyl alcohol (b.p. 78.3°) and isobutyl alcohol (b.p. 106-107°) over alumina at 380-390°.

Alkylation was effected in the apparatus described in our Report V.* The setup is shown in Fig. 1.

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*Cf Report V. 'Alkylation of Isopentane by Propylene', previous article.

50 ml of isopentane and 20 ml of the catalyst were poured into the reactor, after which ethylene or isobutylene was fed from the gas tank via tube 3 while the solution was vigorously stirred by the stirrer (1200-1500 rpm) fitted with a seal. After the run was over, 50 ml of fresh isopentane was gradually added from measuring tank 4; this displaced the old batch of isopentane and the alkylate. In some cases, continuous alkylation was effected in this reactor; the isopentane was then supplied continuously throughout the run via tube 2, the isopentane and the alkylate flowing off continuously to the receiver 6, passing through separator 5 on their way.

When individual tests had to be run with different catalysts, the reactor was disassembled, and the isopentane and the alkylate were separated from the catalyst. The ethylene that did not enter into the reaction was collected in a separate gas tank. After the run was over, the alkylate, dissolved in an excess of isopentane, was washed with water and dried, and the isopentane was driven off in a reactifying tower up to 30°, after which the yield of alkylate in milliliters was determined. The alkylates of several identical tests were combined together and fractionated in a reactifying tower.

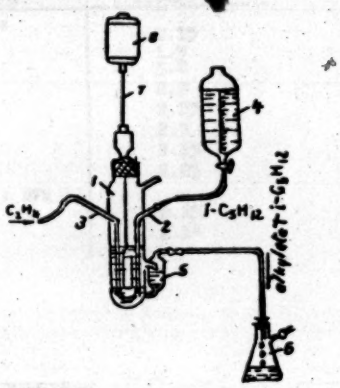

Fig. 1. Continuous-acting reactor for alkylating isopentane with propylene.

1-reactor; 2-supply tube for iso-C_5H_{12}; 3-supply tube for C_3H_8; 4-measuring tank for isopentane; 5-separator; 6-receiver; 7-stirrer; 8-motor.

In Table 1 below we list the results of tests on alkylating isopentane with ethylene and two different liquid catalysts, $0.5P_2O_5 + H_2O + BF_3$, and $0.5P_2O_5 + 1.5H_2O + BF_3$, which were prepared by saturating the corresponding phosphoric acids with boron fluoride [5]. In each run we used 50 ml of isopentane, 20 ml of catalyst, and 4.5 liters of ethylene, which was passed through at the rate of 1.5 liters per hour; the unreacted ethylene was collected in a gas tank.

As the test results indicate, about 50% of the ethylene was converted, although about 5 liters of unreacted gas was collected in the gas tank. This gas was analyzed in an Orsat apparatus for its unsaturated compounds. In Test 1 (first catalyst) the unreacted gas contained 48.0% of unsaturated compounds. Then this same gas sample was analyzed by fractionating it in a Podbielniak apparatus, the following results being obtained: C_2H_4 48.96%, C_5H_{12} 39.1%, C_2H_6 1.5%, C_4H_{10} + + C_4H_8 2.1%, N_2 1.38%, CO_2 0.70%, CO 1.14%, and H_2 4.12%. Thus the unsaturated compounds found in the gas represent unreacted ethylene. Allowing for the ethylene that entered into the reaction, the molar ratio of the isoparaffin to the olefin averaged 1:4.6.

As shown in Table 1, no observable decrease in the activity of the catalyst was found in eight successive tests.

The results of similar tests of the alkylation of isopentane by ethylene with two different catalysts: compounds of boron fluoride with water and with

TABLE 1

Alkylation of Isopentane by Ethylene With Various Catalysts

Test No.	Specific gravity of alkylate d_4^{20}	Alkylate yield		Quantity of unreacted ethylene, liters
		in ml	% of ethylene entering into reaction	
	Catalyst $0.5P_2O_5 + H_2O + BF_3$			
1.	0.688	7.5	181	2:15
2	0.6813	6	100	1:5
3	0.690	6	178	3.0
4	0.690	6.1	181	2.9
5	0.68	7.0	181	2.25
6	0.669	6	163	2.9
7	0.696	7.3	185	2.15
8	0.690	6.5	170	2.25
	Catalyst $0.5P_2O_5 + 1.5H_2O + BF_3$			
1	0.689	7.0	185	2.25
6	0.690	7.4	182	2.14

TABLE 2

Alkylation of Isopentane by Ethylene

Test No.	Specific gravity of alkylate d_4^{20}	Alkylate yield		Quantity of unreacted ethylene, liters
		in ml	% of ethylene entering into reaction	
	Catalyst $H_2O \cdot BF_3$			
1	0:692	7.5	171	2:4
2	0.6381	15	200	1:5
3	0.6840	9	190	2:25
4	0.685	9	190	-
5	0.685	7	141	-
6	0.6769	7	146	-
7	0.6992	7	150	-
	Catalyst $CH_3OH \cdot BF_3$			
1	0.7224	5	170	3.2
2	0.681	3	140	3.8
3	0.680	3	140	-
4	0.679	3.5	150	3.6
	Catalyst $(C_2H_5)_2O \cdot BF_3$ *			
2	-	0	0	4.9.

methanol, are listed in Table 2 above; 5 liters of ethylene, 50 ml of isopentane, and 20 ml of the catalyst were used in each test.

The data of Tables 1 and 2 show that ethylene alkylation is about the same whether $0.5P_2O_5 + 1.5H_2O + BF_3$, $0.5P_2O_5 + H_2O + BF_3$, or $H_2O \cdot BF_3$ is used as the catalyst.

The compound of BF_3 with CH_3OH, which is called methoxy-fluoboric acid, is less active as a catalyst, as indicated by the smaller conversion of ethylene under the same experimental conditions and by the lower yield of alkylate.

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* Pure BF_3 does not cause alkylation either.

The etherate of boron fluoride, $(C_2H_5)_2O \cdot BF_3$, is inactive as a catalyst.

After washing and drying, the alkylates were fractionated in batches of at least 40-50 ml with a rectifying tower with a fractionating ability equivalent to 12 theoretical trays.

TABLE 3

Fractional Composition of Products of Alkylation of Isopentane by Ethylene

Boiling range,°	Volume of fraction, ml	Fractional composition, % by volume	d_4^{20}	n_D^{20}	Remarks
40-50°	6.8	–	0.6270	–	Pentanes
50-60	10	29	0.6410	1.3729	Isohexanes
60-80	1.2	3.5	–	1.3828	–
80-90	4.9	14	0.6887	1.3959	Isoheptanes
90-100	0.9	2.6	0.697	1.3994	–
100-110	1.0	2.9	–	–	–
110-120	3.6	10.4	0.7058	1.4053	
120-130	2.0	5.8	0.7118	1.4120	
130-140	3.2	9.2	0.7234	–	
residue 140.....	5	14.4	–	–	83.5% distilled over up to 140°

Table 3 gives the fractional composition of the products of the alkylation of isopentane by ethylene with a catalyst consisting of boron fluoride and phosphoric acid.

Fractionation curves of the alkylates of isopentane with ethylene, using two different catalysts, are shown in Fig. 2.

The data indicate that in one case an appreciable isohexane fraction is formed together with an isoheptane one. When $H_2O \cdot BF_3$ is used as a catalyst, an isoheptane fra fraction is obtained, but almost no isohexane fraction.

To establish the chemical composition, several alkylate fractions were subjected to spectroscopic analysis by the method of combined light scattering. In analyzing the alkylates of isopentane with ethylene it was found that none of the test samples contained olefins or aromatic and naphthene hydrocarbons, but were mixtures of paraffin hydrocarbons. The results of optical analysis of the heptane and octane fractions are given in Table 4.

One of the first fractions, boiling at 40-50°, was also analyzed. Its composition was:

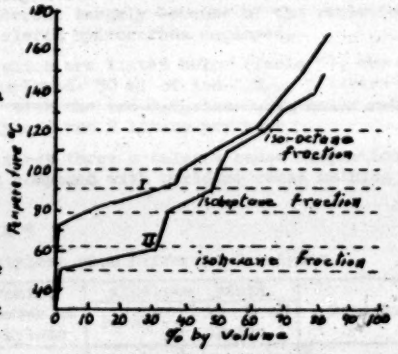


Fig. 2. Fractional composition of the products of alkylation of isopentane by ethylene with different catalysts.

I – $BF_3 \cdot H_2O$;
II – $0.5P_2O_5 + H_2O + BF_3$.

Produced in several identical runs.

Isopentane 72%
n-Pentane 1.7%
2-Methylbutane..... 12%

This fraction contains a considerable amount of isopentane, which could not be entirely removed from the fractions that boiled below 50°; n-pentane is obviously formed from isopentane as the result of isomerization.

TABLE 4

Chemical Composition of the Heptane and Octane Fractions of the Products of the Alkylation of Isopentane by Ethylene

Hydrocarbons	Alkylate composition, in %	
	$0.5P_2O_5 + H_2O + BF_3$	$H_2O \cdot BF_3$
Heptane fraction 80-90°		
2,3-Dimethylpentane	55	48
2,4-Dimethylpentane		37
2,2-Dimethylpentane	33	3
2-Methylhexane		9
Other hydrocarbons	12	3
Octane fraction 100-120°		
2,2-Dimethylhexane	35	70
2,5-Dimethylhexane	—	30
2,2,4-Trimethylpentane	25	—
2,3,3-Trimethylpentane	25	—
Other isomers	15	—

Then experiments were made on the alkylation of isopentane by isobutylene. Investigation of this reaction is of interest largely because of the variation of the nature of the reaction with the olefin hydrocarbon employed.

In the experiments, the results of which are listed below (Table 5), the following quantities of reagents were employed: 50 ml of iso-C_5H_{12}, 5 liters of iso-C_4H_8, and 20 ml of liquid catalyst, with the iso-C_4H_8:iso-C_5H_{12} molar ratio at 1:2. The rate of feed of the isobutylene was 2 liters per hour.

Experimental results show that the first three catalysts cause alkylation whereas boron fluoride etherate and its compound with pyridine cause nothing but polymerization.

TABLE 5

Alkylation of Isopentane by Isobutylene with Different Catalysts

Catalyst	Specific gravity of alkylate	Bromine number of alkylate	Alkylate yield		Remarks
			in ml	In % of olefin	
$0.5P_2O_5 + 1.5H_2O + BF_3$	0.7546	1.2	21	180	Alkylation takes place
$0.5P_2O_5 + H_2O + BF_3$...	0.7198	1.6	27	220	
$H_2O \cdot BF_3$	0.7201	1.5	25	205	
$(C_2H_5)_2O \cdot BF_3$	0.7307	24	13	108	Polymerization takes place
$C_5H_5N \cdot BF_3$	0.7286	21.4	12	100	

This indicates the specificity of the alkylation and polymerization reactions, which take place according to different mechanisms: it is not enough for a catalyst to be able to cause polymerization for it to make alkylation possible under the same conditions.

Table 6 gives the fractional composition and the physical and chemical properties of the various fractions.

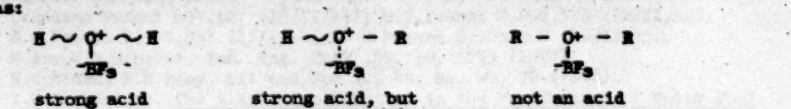
TABLE 6

Fractional Composition of the Product of the Alkylation of Isopentane by Isobutylene

Boiling range, °	Volume of fraction, ml	Fractional composition, % by volume	d_4^{20}	n_D^{20}	Remarks
30-40°	6.4	–	0.6280	–	
40-50	2	–	–	–	
50-60	0	–	–	–	
60-70	0.4	1.1	–	–	
70-80	0.2	0.8	–	–	
80-90	0.3	0.85	0.6770	1.3782	
90-100	0.4	1.1	0.6901	1.3900	
100-110	1.1	3.1	0.7015	1.3945	Iso-octanes 9.3%
110-120	2.2	6.2	0.7057	1.3998	
120-130	2.4	6.8	0.7115	1.4038	
130-140	3	8.5	0.7178	1.4051	Isononanes 26.8%
140-150	4	11.3	0.7275	1.4061	
150-160	2.4	6.8	0.7353	1.4151	
160-170	3	8.5	0.7422	1.4191	65% distills up to 170°
residue 170	11	31.2	0.7972	1.4473	

The fractional composition indicates that alkylation produces only a fairly small quantity of the expected isononane hydrocarbons.

The experimental results of the alkylation of isopentane by ethylene and isobutylene corroborate the behavior patterns set forth by us earlier in other connections [10], to wit, that the only active catalysts in the alkylation of the isoparaffins are compounds of BF_3 with substances that contain hydroxyl groups. The molecular compounds of BF_3 with ethers and esters, as well as with amines, are catalytically inactive. These laws are related to the nature of boron fluoride compounds. As conductivity measurements indicate, the hydrates of BF_3 ($H_2O \cdot BF_3$ and $BF_3 \cdot 2H_2O$) and its compounds with alcohols ($ROH \cdot BF_3$) are strong acids, whereas the etherates of BF_3 are not acids according to their conductivities. In the molecular compounds of BF_3 with acids, the acidity is much higher than that of the initial acids. The manifestation of acidity in some BF_3 compounds and its increase in others are due to a weakening of the bond between the proton and the oxygen atom in molecular compounds as the result of the shift of the oxygen atom to a trivalent positive level and the accumulation of electronegative groups within the molecule, as is illustrated by the following structural formulas:



strong acid (I)

strong acid, but weaker than (I) (II)

not an acid (III)

As we know, compounds of BF_3 with substances containing oxygen are formed by the oxygen atom giving up an electron, becoming trivalent positive, and the boron atom absorbing an electron, becoming quadrivalent negative.

Thus, compounds of BF_3 with substances containing hydroxyl are strong acids, and catalysis in an alkylation reaction is then explainable as ordinary acid catalysis.

SUMMARY

1. The catalytic alkylation of isopentane by ethylene and isobutylene with a number of catalysts based upon boron fluoride has been studied. The assertion made by the authors of this paper in connection with other instances of alkylation has been confirmed, namely, that only compounds of BF_3 with compounds containing hydroxyl and with acids are active in low-temperature catalytic alkylation. Acids as such (HF, H_2SO_4, H_3PO_4) do not bring about alkylation by ethylene without BF_3.

2. Alkylation of isopentane by ethylene with the catalysts P_2O_5, H_2O, BF_3, and $H_2O \cdot BF_3$ occurs at atmospheric pressure, though at a reduced rate. The alkylate yield is 160-200% in terms of the initial ethylene, with the specific gravity of the alkylate at 0.69. The alkylation of isopentane by isobutylene takes place at a rapid rate, with a yield of 180-220% in terms of the initial isobutylene, a sp. gr. of 0.71-0.72, and a bromine number of 1-1.5.

3. The chemical composition of the alkylates was investigated by the method of combined light scattering. The alkylate consists of a mixture of hexanes, heptanes, octanes, and hydrocarbons of higher molecular weight. The heptane fraction of the products of the alkylation of isopentane by ethylene consists of dimethylpentanes; no trimethylbutane is formed. In the alkylate of isopentane with isobutylene, the nonane fraction represents about 25% by volume of the total.

4. The alkylation of the isopentane by ethylene is of no industrial interest, since isopentane is a component of motor fuel, whereas the hydrocarbons formed in the alkylate (dimethylpentanes) have a lower octane number than the initial isopentane. Research on this reaction is of theoretical interest in connection with study of the activity of various catalysts.

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THERMOCHEMICAL RADII AND ENERGY OF TETRAHEDRAL AND TRIANGULAR IONS

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The notion of the thermochemical radius of an ion was first proposed in 1934. The thermochemical radius of an ion is defined as the value of the radius computed from energy characteristics (lattice energy of a salt, entropy of an ion in a solution, etc.) [1].

Later on, this concept was extended to nonspherical ions, the thermochemical radius then being taken to mean the radius of a hypothetical spherical ion that could replace the given ion isoenergetically in the crystal lattice. Development of different variants of methods of computing thermochemical radii made it possible to find the thermochemical radii of dozens of ions and to solve a number of the energy problems of polyatomic and complex ions [2,3,4].

But the relationship between the crystallochemical properties of a nonspherical ion (its form and dimensions) and the magnitude of its thermochemical radius had not been established.

Before taking up the solution of this problem, let us deal in somewhat greater detail with some peculiarities of the thermochemical radii of polyatomic ions, which have received inadequate treatment in the literature.

The thermochemical radii of ions of the RO_n^{z-} type is characterized by the same constancy as their crystallochemical radii, found from the data of X-ray analysis. To illustrate this point, we cite below the thermochemical radii of NO_3^-, ClO_3^-, HCO_3^-, SO_4^{--}, CrO_4^{--}, and O_2^- in a number of different salts (Table 1). These values were computed by means of the Kapustinsky equation [10] for the lattice energy of a salt:

$$U = 287.2 \frac{\sum n z_1 z_2}{r_1 + r_2} \left(1 - \frac{0.345}{r_1 + r_2}\right) . \qquad (1)$$

The value of U was found from thermochemical data (the difference between the heat of formation of the solid salt and that of the gaseous ions [5,11]), the cation radii being taken from Goldschmidt's figures [1].

Analysis of the data listed indicates that the fluctuations in the size of the thermochemical radii of the ions in question usually do not exceed the fluctuations in the size of the ion radii calculated from the analysis of X-ray structure data.

Furthermore, the existence of a definite relationship between the size of the anion's thermochemical radius and the size of the cation is worthy of note: as the size of the ion of opposite charge increases, the thermochemical radius of the given nonspherical ion also increases. The changes in the thermochemical radius of the ion are hardly as much as two per cent, but their existence is indisputable.

Table 1

Compounds	Thermochemical radius of the anion	Compounds	Thermochemical radius of the anion	Compounds	Thermochemical radius of the anion
Ion NO_3^-		Ion ClO_3^-		Ion SO_4^{--}	
$NaNO_3$	1.89	$NaClO_3$	2.01	$CaSO_4$	2.28
KNO_3	1.89	$KClO_3$	2.00	$SrSO_4$	2.31
$RbNO_3$	1.89	$RbClO_3$	1.98	$BaSO_4$	2.31
$CsNO_3$	1.86	$CsClO_3$	1.99	$[Co(NH_3)_5NO_2]SO_4$	2.33
$Ca(NO_3)_2$	1.88	$Sr(ClO_3)_2$	2.00	$[Co(NH_3)_5Cl]SO_4$	2.33
$[Mg(H_2O)_6](NO_3)_2$	1.86	$Ba(ClO_3)_2$	2.02	$[Co(NH_3)_5Br]SO_4$	2.32
$[Ca(H_2O)](NO_3)_2$	1.87	$[Ba(H_2O)]ClO_3)_2$	2.01		
$Sr(NO_3)_2$	1.88	$[Ni(H_2O)_6](ClO_3)_2$	2.05	Ion CrO_4^{--}	
$Ba(NO_3)_2$	1.89	$[Ni(NH_3)_6](ClO_3)_2$	2.03		
$[Ca(H_2O)_2](NO_3)_2$	1.86			$BaCrO_4$	2.39
$[Ca(H_2O)_4](NO_3)_2$	1.87	Ion HCO_3^-		$[Co(NH_3)_5NO_2]CrO_4$	2.42
$[Sr(H_2O)_4](NO_3)_2$	1.88			$[Co(NH_3)_5Cl]CrO_4$	2.41
$[Ni(H_2O)_6](NO_3)_2$	1.88	$NaHCO_3$	1.58	$[Co(NH_3)_5Br]CrO_4$	2.37
$[Mg(H_2O)_6](NO_3)_2$	1.90	$KHCO_3$	1.57		
$[Co(H_2O)_6](NO_3)_2$	1.90	$Ca(HCO_3)_2$	1.58	Ion O_2^{--}	
$[Zn(H_2O)_6](NO_3)_2$	1.90	$Sr(HCO_3)_2$	1.60		
$[Ca(H_2O)_8](NO_3)_2$	1.90	$Ba(HCO_3)_2$	1.60	CaO_2	1.80
$[Co(NH_3)_5Cl](NO_3)_2$	1.94	$[Zn(NH_3)_6](HCO_3)_2$	1.56	SrO_2	1.80
$[Co(NH_3)_5Br](NO_3)_2$	1.93	$[Cu(NH_3)_6](HCO_3)_2$	1.60	BaO_2	1.79

We shall confine ourselves to a discussion of the cases in which there is no free rotation of the polyatomic ions. The phenomenon described above may be explained as due to the fact that a large cation effects a smaller penetration into the 'hollow' of a nonspherical anion. This 'penetration effect' of small cations results in an appreciable diminution in the thermochemical radius of a nonspherical anion. This effect is illustrated in the accompanying figure for the sake of clearness.

Geometrical calculation shows that when the dimensions of the 'outer' ion are about equal to or exceed the dimensions of the X atoms in the RX_n^{z-} anion, the 'penetration effect' has little influence upon the size of the thermochemical radius. If the outer ions are smaller than the X atoms, the 'penetration effect' becomes appreciable. This makes it easy to explain the lack of constancy in the thermochemical radii of the anions in lithium and magnesium salts [2].

The existence of the 'penetration effect' may also explain several seeming anomalies in the sequence of the heats of hydration of salts.

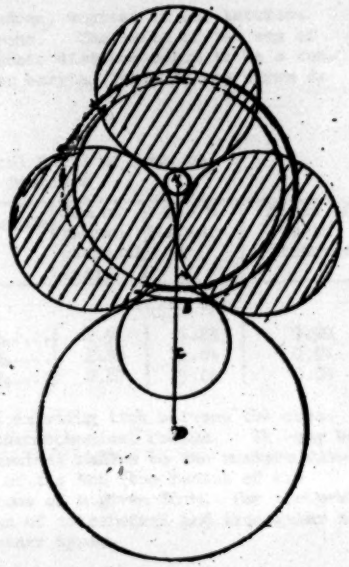
The heat of hydration of an anhydrous salt (Q) may be found from the equation:

$$Q = U_k - U + W, \qquad (2)$$

where U_k is the lattice energy of the aquo-salt, U is the lattice energy of the initial salt, and W is the heat of formation of the gaseous aquo-ion from the gaseous central ion and the gaseous water molecules. Salts with the same aquo-cation have the same value of W, and the sequence of the heats of hydration is governed by the differences in the lattice energies, i.e., it rises with an increase in the dimensions of the anion for salts with inert-gaseous cations.

This conclusion is fully confirmed in the case of spherical anions (F^-, Cl^-, Br^-, and I^-), but the situation is somewhat more complicated in polyatomic anions. For example, the heat of hydration of nitrates ought to be higher than the heat of hydration of the corresponding chlorides (the radius of NO_3 is 1.89 Å, and that of Cl^- is 1.81 Å), but actually it is lower. A similar anomaly is observed in the case of chlorates and bromides (the respective ion radii are 2.00 and 1.96 Å). These seeming anomalies are due to the fact that the 'penetration effect' is diminished when a larger aquo-cation is combined with a polyatomic anion, which results in a relative increase in the difference between the lattice energies as against that prevailing in the halides. Examples that illustrate this phenomenon are listed in Table 2.

The thermochemical radius of a nonspherical ion equals neither the maximum distance from its center to the surface (radius of the circumscribed sphere) nor the minimum distance of the maximum penetration, but is some mean value between these two figures. For instance, the thermochemical radius of the O_2^{--} anion is 1.80 Å; this ion is an ellipsoid of revolution with semiaxes of 1.98 and 1.24 Å, [6].



NB-thermochemical radius of the anion; DB-radius of a large cation; CB-radius of a small cation; AB-diminution of the thermochemical radius due to the 'penetration effect'.

Table 2

Heats of Hydration of Some Anhydrous Salts

Compound formed by adding water	Heat of hydration, cal.	Compound formed by adding water	Heat of hydration, cal.
$[Li(H_2O)_3]Cl$	42.3	$[Ca(H_2O)](NO_3)_2$	14.0
$[Li(H_2O)_3]NO_3$	40.0	$[Ca(H_2O)_4]Cl_2$	58.4
$[Mg(H_2O)_2]Cl_2$	36.9	$[Ca(H_2O)_4](NO_3)_2$	54.4
$[Mg(H_2O)_2](NO_3)_2$	28.8	$[Ba(H_2O)]Br_2$	16.6
$[Mg(H_2O)_6]Cl_2$	96.5	$[Ba(H_2O)](ClO_3)_2$	14.4
$[Mg(H_2O)_6](NO_3)_2$	89.0	$[Ba(H_2O)]Cl_2$	15.3
$[Ca(H_2O)]Cl_2$	16.8	$[Ba(H_2O)](IO_3)_2$	12.7

It is not difficult to prove that the thermochemical radius of an ion may be calculated from the measured distances between the central atom of the complex ion and the metal cations. In fact, this distance cannot equal the sum of the thermochemical radii of the ions in the general case, as our thermochemical radii

have been computed for the surrounding octahedron, whereas in the lattices studied, the surroundings may be quite different. The ratio of the sum of the thermochemical radii to the actual interionic distance ought to be a constant. Salts that crystallize like calcite or baryta (Table 3) may serve as examples of this kind of constant ratio.

Table 3

Ratio of the Sum of the Thermochemical Radii of Ions to Their Actual Interionic Distance

Compounds	Sum of thermochemical radii	S - O distance, Å	Ratio of sum to distance	Compounds	Sum of thermochemical radii	S - O distance, Å	Ratio of sum to distance
Baryta type				Calcite type			
$BaSO_4$....	3.73	3.54	1.05	$CaCO_3$....	2.91	3.23	0.90
$SrSO_4$....	3.57	3.39	1.05	$MnCO_3$....	2.76	3.04	0.91
$PbSO_4$....	3.62	3.41	1.06	$NaNO_3$....	2.87	3.24	0.89

The data of Table 3 indicate a doubtless existing link between the crystalline characteristics of the ion and its thermochemical radius. It may be assumed that the ratio of the ion's thermochemical radius to the maximum distance from the center to the farthest point of the ion (the radius of the circumscribed sphere) will be constant for ions of a given form. For the present we shall confine ourselves to a consideration of tetrahedral and triangular ions, owing to the inadequacy of data on ions of other types.

Table 4

Ratio of Thermochemical Radii to the Radius of the Circumscribed Spheres

Ion	Thermochemical radius	Radius of the circumscribed sphere	Ratio	Ion	Thermochemical radius	Radius of the circumscribed sphere	Ratio
Triangular ions				MnO_4^-	2.40	3.10	0.79
NO_3^-	1.89	2.79	0.67	HF_4^-	2.28	2.86	0.80
CO_3^{--}	1.85	2.79	0.66	SO^{--}	2.30	2.94	0.78
Tetrahedral ions				CrO_4^{--}	2.40	3.16	0.76
ClO_4^-	2.36	2.90	0.81	MoO_4^{--}	2.54	3.26	0.78

Table 4 gives the thermochemical radii* and the radii of the circumscribed spheres for the two designated types of ions. The ratio of these two quantities is actually constant for ions of the given form, namely: 0.67 for triangular ions, and 0.79 $\pm$ 0.03 for tetrahedral ions (including deformed tetrahedrons).

The existence of such a simple relationship between the radius of the circumscribed sphere and the thermochemical radius of the ion enables us to calculate the thermochemical radii of a series of other ions with analogous structure (BO_3^{---}, BeF_4^{--}, IO_4^-, SeO_4^{--}, TeO_4^{--}, PO_4^{---}, AsO_4^{---}, SbO_4^{---}, BiO_4^{---}) in so far as their forms and the radii of their circumscribed spheres are known. These thermochemical radii are listed in Table 5.

It is worthwhile to compare the thermochemical radii of triangular and

---

*The thermochemical ion radii listed in Table 4 were found from the differences in the heats of formation of their salts with the given anion [1].

Table 5

Thermochemical Ion Radii, Computed from Crystallochemical Data

Ion	Radius of circumscribed sphere	Thermochemical radius	Ion	Radius of circumscribed sphere	Thermochemical radius
BO_3^{---}...	2.86	1.91	PO_4^{---}	3.01	2.38
BeF_4^{--}...	3.10	2.45	AsO_4^{---}	3.14	2.48
IO_4^-	3.15	2.49	SbO_4^{---}	3.29	2.60
SeO_4^{--}...	3.07	2.43	BiO_4^{---}	3.40	2.68
TeO_4^{--}	3.22	2.54			

tetrahedral ions with their positions in the Periodic Table. This sort of comparison is made in Table 6.

This comparison indicates that in a given period the thermochemical radii of ions of the same form are approximately constant, with some tendency for them to drop as the atomic number rises. Within the groups of the Periodic Table, the thermochemical radii of ions of similar structure increase regularly with increasing atomic number.

Knowing the thermochemical radii of ions makes it possible to solve a number of important energy problems. In particular, this quantity enables us to find the heats of formation of gaseous ions by at least two methods.

If the heat of formation of any crystalline salt with the given ion (with the exception of the M_2X and M_3X types) is known, we can find the heat of formation of the gaseous ion from the equation:

$$-\Delta H_A = \Delta H_K - \Delta H_{KA} - U_{KA} \qquad (3)$$

where ΔH_A, ΔH_K, and ΔH_{KA} are the heats of formation of the gaseous anion, the gaseous cation, and the solid salt, respectively, and U_{KA} is the lattice energy of the given salt, computed from the Kapustinsky equation, using the thermochemical radii of the ions. We calculated the heats of formation of gaseous ions of the metals from the latest data on the ionization potentials and the heats of sublimation of metals [8,12].

Here, as later on, the heats of formation of solid salts have been taken from the summaries published by E. Britske and Kapustinsky [5]. Substituting these values in Equation (3), we found the heats of formation of the following gaseous ions: NO_3^-, ClO_3^-, ClO_4^-, MnO_4^-, CO_3^{--}, SO_4^{--}, CrO_4^{--}, SeO_4^{--}, MoO_4^{--}, WO_4^{--}, BO_3^{---}, PO_4^{---}, AsO_4^{---}, and SiO_4^{----} (Table 7). To compute the heat of formation of the gaseous ion IO_4^- we determined the hitherto unknown heat of formation of crystalline $NaIO_4$ experimentally (cf Experimental Section).

On the other hand, it has been shown [4] that the thermochemical radius of an ion is directly related to its heat of hydration. If the heat of formation of the given ion in an aqueous solution and its thermochemical radius are known, we can compute the heat of formation of the gaseous ion from the heat of hydration. The heats of formation of the gaseous ions FeO_4^{--} and SbO_4^{---} (Table 7). were found in this manner.

It follows from the data of Table 7, moreover, that for anions carrying two and three charges, the heat of hydration of an anion with a given charge is

Table 6

Comparison of the Anion Radii in the Periodic Table

Periods	Groups				
	III	IV	V	VI	VII
2	BO_3^{---} 1.91	CO_3^{--} 1.85	NO_3^- 1.89	–	–
3	–	SiO_4^{----} 2.40	PO_4^{---} 2.38	SO_4^{--} 2.3	ClO_4^- 2.36
4	–	–	–	CrO_4^{--} 2.4	MnO_4^- 2.40
4	–	–	AsO_4^{---} 2.48	SeO_4^{--} 2.43	–
5	–	–	–	MoO_4^{--} 2.54	–
5	–	–	SbO_4^{---} 2.60	TeO_4^{--} 2.54	IO_4^- 2.49

Table 7

Thermochemical Radii Heats of Formation in the Gaseous State and Heats of Hydration of Ions *

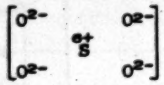
Ions	Thermo-chemical radii	Heats of formation in the gaseous state	Heats of hydration	Ions	Thermo-chemical radii	Heats of formation in the gaseous state	Heats of hydration
NO_3^-	1.89	80.0	70.7	MoO_4^{--}	2.54	230	216
ClO_3^-	2.00	57.8	64	TeO_4^{--}	2.54	155	(216)
ClO_4^-	2.36	91.5	50	WO_4^{--}	2.57	266	202
MnO_4^-	2.40	174	49	BO_3^{---}	1.91	-240	760
IO_4^-	2.49	99	(40)	PO_4^{---}	2.38	50	550
CO_3^{--}	1.85	47	317	AsO_4^{---}	2.48	-20	530
SO_4^{--}	2.3	178	241	SbO_4^{---}	2.60	-20	(515)
CrO_4^{--}	2.4	182	229	SiO_4^{----}	2.4	(-350)	–
SeO_4^{--}	2.43	124	224				

* In contradistinction to our prevous papers [4] we here adopt the division of heads of hydration of the cation and the anion proposed by Mishchanko [7] in all computations the heat of hydration of the potassium ion being taken as 80 Cal.

governed by the size of its thermochemical radius.

The values of the heats of formation of gaseous ions computed by us make it possible to approach a solution of the problem of the types of chemical bond in the ions under consideration.

The sulfate ion, for example, can be imagined as constructed of the S^{6+} and O^{2-} ions in accordance with Kossel's diagram:



or of S^{2+} and O^{-} ions, with four covalent S — O bonds, in accordance with Lewis' diagram:

In actuality, it appears, several structures are superposed, including structures with double bonds, which are not dealt with here.

If we assume that the basic, predominant structure in the sulfate ion is the Kossel one, the heat of formation of $SO_4^{--}(g)$ may be computed from the following process:

$$S^{6+}_{(g)} + 4O^{2-}_{(g)} = SO_4^{--}(g) + W_1,$$

where W_1 is a quantity that can be calculated from the following equation:

$$W_1 = k\,N\,e^2 \cdot \left[\frac{z_K z_A^n}{r}\,(1-\delta) - S_p\,\frac{z^2 A}{r}\,n\right]. \qquad (4)$$

In this equation, z_K and z_A are the charges on the cation and anion, respectively (in the given case, $z_K = 6$, and $z_A = 2$); n is the number of anions (here $n = 4$); r is the distance between the centers of ions of opposite charge; δ is the repulsive term, taken by us as 0.22; S_p is the 'screening factor,' 0.92 for tetrahedral ions and 0.58 for triangular ions; N is the Avogrado number; e is the charge on an electron; and k is a conversion factor to express W_1 in large calories.

If we take the experimental value of r (1.61 Å, we get a value of 4660 Cal for W_1, whereas the energy of process (1) is found to be 7340 Cal from the value of the heat of formation of $SO_4^{--}(g)$ computed by us (we shall henceforth call this the 'experimental' value), in this case, therefore, the difference is as much as 2700 Cal. Hence, the Kossel structure plays no appreciable role in the sulfate ion.

The energy of formation of the Lewis structure may be computed from the process:

$$S^{2+}_{(g)} + 4O^{-}_{(g)} = SO_4^{--}_{(g)} + W_2. \qquad (5)$$

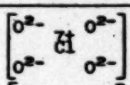
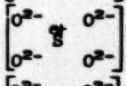
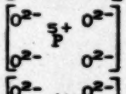
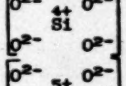
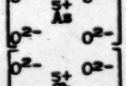
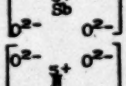
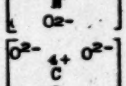
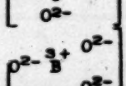
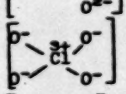
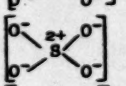
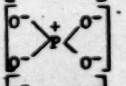
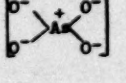
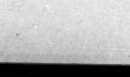
The energy of this process may (W_2) be evaluated from the equation:

$$W_2 = W_1 + mD_{K\text{-}O},$$

where W_1 is the coulomb term, computed from Equation (4) (here $z_K = 2$ and

Table 8

Structure and Energy of Formation of Anions

Ions	Assumed Structure	Energy, computed from Equations (4) and (5), Cal.	Experimental value of W, Cal.	Difference, Cal.
ClO_4^-		6050	10050	4000
SO_4^{--}		4660	7340	2680
PO_4^{---}		3240	4780	1540
SiO_4^{----}		1980	2950	970
AsO_3^{---}		2980	4590	1610
SbO_4^{---}		2760	4350	1590
BO_3^-		3800	6930	3130
CO_3^{--}		2640	4200	1760
BO_3^{---}		1530	2140	610
ClO_4^-		1390	1820	430
SO_4^{--}		725	1000	275
PO_4^{---}		90	280	190
SiO_4^{----}		-356	-350	6
AsO_4^{---}		60	190	130

$z_A = 1$, while all the other variables have the same significance as before); and D_{K-O} is the energy of the covalent bond between the central atom of the anion and the oxygen. On the basis of the Pauli approximations we have computed the energy of the covalent bond to be 49 Cal for the S – O bond.

Employing Equation (5), we found $W_2 = 725$ Cal, whereas our data give $W_2 = 1000$ Cal, i.e., the difference is 275 Cal in this case. Thus, our data definitely indicate that the Lewis structure is among the most probable for the SO_4^{--} ion.

We made analogous calculations for a number of other ions.

The data listed in Table 8 indicate that the Kossel structure is also highly improbable for the other ions examined by us, the structures with single-charge anions of oxygen and covalent bonds being much more likely.

As was to have been expected, the Kossel structures become more probable as the oxidation state of the central atom is lowered, though they are not appreciably represented in a single one of the cases considered.

EXPERIMENTAL *

The heat of formation of crystalline sodium metaperiodate ($NaIO_4$) was determined by measuring the heat of solution of this salt in water. The initial product was prepared and purified by the method described by Kirkpatrick and Dickinson [8]. The purity of the prepared $NaIO_4$ was checked by analysis for the per cent of iodine.

All measurements were made in a calorimeter, consisting of a 1-liter Dewar flask immersed almost to the top in a thermostat at a temperature of 25°. Temperatures were read from a Beckmann thermometer with a full-scale range of 1° The precision of readings was ± 0.0005°. The water equivalent of the calorimeter and the specific heats of the solutions were determined by the method described by Brevsky and Kaigorodova [9].

The extremely slow dissolution of the $NaIO_4$ is worthy of note; as a result, the principal period lasted 12 minutes. All the required corrections were made graphically. The test results are listed in Table 9.

Table 9

Heat of Solution of $NaIO_4$ in Water

Weight, g	Dilution	Change in temperature (°), corrected for radiation	Radiation correction	Calorimeter thermal capacity, cal	Heat of solution, cal	Mean value, cal.
2.4474	2430	-0.1830	0.0020	561.6	-8960	-8910
3.0857	830	-0.2276	0.0052	562.2	-8870	

The heat of formation of $NaIO_4$ in aqueous solution is 95.1 Cal (the sum of the heats of formation of the Na^+_{aq} and the $IO_4^-{}_{aq}$ ions in aqueous solution [5]. Using this figure and the value of the heat of solution of the salt as found by us, we found $\Delta H°_{298} = -104.0$ Cal for crystalline $NaIO_4$.

SUMMARY

1. The constancy of the thermochemical radii for polyatomic nonspherical ions has been established. The negligible deviations may be explained by the 'penetration effect', i.e., the partial entrance of the ion of opposite charge

* The experiments werecarried out in the Ivanovo Institute of Chemical Engineering.

into the hollow existing in the nonspherical ion.

2. A relationship has been established between the crystallochemical properties of tetrahedral and triangular ions and their thermochemical radii, namely: for ions of a given form, the ratio of the thermochemical radii to the radii of the circumscribed spheres is a constant.

3. The thermochemical radii, the heats of formation in the gaseous state, and the heats of hydration have been computed for the following ions: MnO_4^-, IO_4^-, CO_3^{--}, SO_4^{--}, CrO_4^{--}, SeO_4^{--}, MoO_4^{--}, TeO_4^{--}, WO_4^{--}, BO_3^{---}, PO_4^{---}, AsO_4^{---}, SbO_4^{---}, and SiO_4^{----}. A relationship has been shown to exist between the magnitude of the thermochemical radii of ions and the position of the elements constituting the given ions in Mendelyeev's Periodic Table.

4. The unreality of Kossel structures has been demonstrated for ions of the RO_n^{z-} type.

5. The heat of formation of $NaIO_4$ has been determined experimentally, and the heat of formation of this compound under standard conditions computed ($\Delta H^\circ_{298} = -104.0$ Cal).

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*An apparent typographical error.

A NEW METHOD OF SYNTHESIZING AMIDES OF CARBOXYLIC ACIDS DIRECTLY FROM THE ACIDS

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The complete amide of sulfuric acid, or the sulfamide ($NH_2SO_2NH_2$), is gradually hydrolyzed when heated in aqueous acid or alkaline solutions [1], being converted into ammonia and sulfamic acid (NH_2SO_2OH), which yields sulfuric acid and another molecule of ammonia upon further hydrolysis.

By analogy, it might have been expected that the acidolysis of sulfamide in the absence of water ought to yield sulfamic acid and the amide of the corresponding acid, as follows:

$$\begin{matrix} NH_2SO_2NH_2 \\ HOCOR \end{matrix} \longrightarrow NH_2SO_2OH + NH_2COR \qquad (I)$$

Preliminary experiments confirmed this conjecture, indicating that when sulfamide is reacted with carboxylic acids, amides of the carboxylic acids are actually produced.

The conversion of carboxylic acids into their amides directly, without any intermediate stages, is no doubt of considerable theoretical and practical interest, and we therefore undertook a more detailed investigation of this reaction.

It was found that the amidation of carboxylic acids by sulfamide takes place at relatively low temperatures, under mild conditions, and thus it may be employed to amidate carboxylic acids that decompose fairly readily upon heating.

Up to the present time, the direct conversion of carboxylic acids into their amides has been observed in the reaction of carboxylic acids with the amides of other carboxylic acids and in the reaction of carboxylic acids with amides of aromatic and aliphatic sulfonic acids, as follows:

$$RCOOH + R'CONH_2 \rightleftharpoons RCONH_2 + R'COOH \qquad (II)$$

$$RCOOH + R'SO_2NH_2 \longrightarrow RCONH_2 + R'SO_2OH \qquad (III)$$

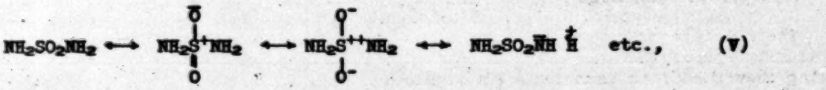
Reaction (II), which resembles the acidolysis of esters, has been the object of but little research [2]. This reaction is apparently unsuitable as a general method of preparing amides of acids, if we are to judge by the data available in the literature, as it is an equilibrium reaction, takes place under severe conditions, and affords low yields.

Reaction (III) has been the subject of rather detailed study by Oxley [3]; it is of theoretical as well as practical interest, as it makes possible the synthesis of amides of carboxylic acids directly from the acids in some cases, with satisfactory yields. Unfortunately, this reaction takes place only at rather high temperatures, and hence

can be employed to amidate only those carboxylic acids that are thermally stable; it cannot be used for carboxylic acids that decompose below 200-250°. Thus, no method has been known up to the present time for converting carboxylic acids directly into amides under mild conditions.

Depending on the structure of the carboxylic acids and of the sulfamide:

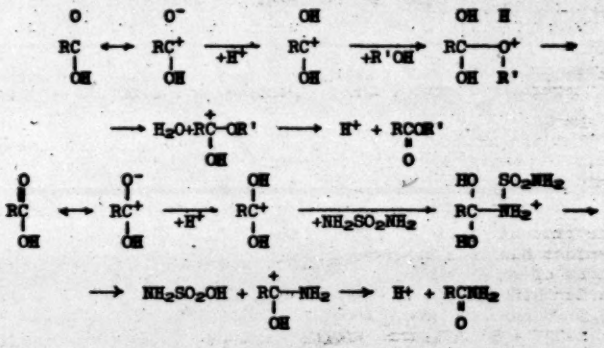
(IV)



(V)

the amidation of carboxylic acids by sulfamide may take place along various lines.

The most probable reaction mechanism is analogous to the mechanism of the esterification of carboxylic acids [4], the nitrogen atom of the sulfamide playing the role of the oxygen atom in the alcchol. Thus, the initial addition product is formed by the interaction of the positively charged carbon atom of the carboxylic acid with the nitrogen atom of the sulfamide, which shifts to a quadrivalent, singly-charged state. This analogy is evident from the following diagram:



(VI)

The source of protons for the formation of the initial active intermediate ion with positive carbon may at first be the very acid to be amidated, and later the sulfamic acid.

Benzoic acid was selected for an experimental study of the amidation of carboxylic acids by sulfamide. We first experimented with the interaction of benzoic acid with sulfamide in aqueous solutions, without the addition of alkali, and then with the addition of various amounts of carbonate and caustic alkalis, as well as tertiary bases. The experiments were run: at room temperature, with heating, with boiling, and at 120° in sealed tubes. In no case were we able to detect the formation of benzamide. The reaction products included: sulfuric acid, unchanged benzoic acid, sulfamic acid, ammonia, and unchanged sulfamide. Evidently, the acidolysis of sulfamide does not take place in aqueous solutions or else takes place at a rate incomparably slower than that of the competing

reaction – the hydrolysis of sulfamide. It should be noted that no study was made of the reaction in aqueous solutions with 'bound' water, i.e., in saturated solutions of sodium chloride, calcium chloride, etc.

The next series of experiments was devoted to the interaction of benzoic acid and sulfamide without any solvent. When an equimolecular mixture of benzoic acid and sulfamide is carefully heated, the reaction mass gradually liquefies, becoming completely transparent at 110°; two layers are formed: the lower one being a solution of benzoic acid in sulfamide, and the upper one being a solution of sulfamide in benzoic acid. At 125° a reaction takes place slowly, as may be noted by the gradual separation of high-melting crystals in the lower layer, which solidifies entirely within a few hours. At higher temperatures the reaction is faster, but the reaction mass turns brown noticeably.

The reaction products were found to contain 10-50% of the theoretical quantity of benzamide, 80-50% of the initial amount of unreacted benzoic acid, 10-50% of benzonitrile, traces of sulfamic acid, some sulfamide, and a considerable quantity of products of the thermal decomposition of sulfamide.

Thus, when benzoic acid and sulfamide are fused together without a solvent, the reaction proceeds smoothly enough in the desired direction, and is accompanied by other reactions that diminish the benzamide yield; for this reason, this reaction will be the subject of further study in one of our subsequent papers.

In the next series of experiments benzoic acid was amidated with sulfamide in the presence of anhydrous pyridine or in a solution of anhydrous pyridine. After a series of preliminary experiments, we succeeded in fixing upon conditions that enabled us to achieve a yield of 84% of the theoretical quantity of benzamide, which is quite satisfactory.

To obtain the best yields it was found to be necessary to use an excess of sulfamide in the reaction, as much of it undergoes thermal decomposition under the reaction conditions, with another portion entering into a side reaction, which itself is of considerable interest and will be the subject of one of our subsequent papers.

The amidation reaction may be completed in 15-20 minutes by heating a mixture of 0.01 mole of acid with 0.02 mole of sulfamide and 5 ml of anhydrous pyridine with a reflux condenser to 125° over an oil bath, but the highest yields are obtained by heating the same mixture for three hours over a boiling water bath. Approximately the same conditions proved to be quite satisfactory for the amidation of other acids as well: p-nitrobenzamide is obtained with a yield of about 95% of theory; m-nitrobenzamide with a yield of 84%; o-chlorobenzamide with a yield of some 85% of theory; p-chlorobenzamide with a yield of 96% of theory; acetamide with a yield of 84% of theory; caprylamide with a yield of 80% of theory; palmitamide with a yield of some 82% of theory; and phenylacetamide with a yield of 70% of theory.

Thus, the reaction of sulfamide with the simplest carboxylic acids in pyridine solution makes it possible to convert the acids into the corresponding amides under mild conditions and with good yields, avoiding the formation of any intermediate products whatsoever. Inasmuch as this reaction results in the formation of amides of acids directly from the acids, it is appropriately called amidation, to distinguish it from the well-known Chichibabin and Zeide reaction, which should be called amination.

We ran many experiments to substitute amides of aromatic sulfo acids for sulfamide, but it was found that these amides cannot serve as an amidating agent

under the mild reaction conditions that suffice for sulfamide amidation. Only at 200-250° do the amides of aromatic sulfo acids amidate carboxylic acids. Our experiments in this field fully corroborate the data of Oxley and Short and their co-workers, [3].

At the present time we are investigating the amidation of other acids: dibasic carboxylic acids, hydroxy acids, amino acids, and sulfo acids, as well as amidation with alkylated sulfamides, etc., all of which will be reported in subsequent papers.

EXPERIMENTAL

Experiments on the Amidation of Benzoic Acid by Fusing It with Sulfamide Without Any Solvent

0.01 mole of benzoic acid (1.22 g) was mixed in a test tube with 0.01 mole of sulfamide (0.96 g), and the mixture was gradually heated over an oil bath while it was continuously stirred with a thermometer. At 100° the mixture was observed to liquefy, and at 110° it became completely transparent, two layers forming. Samples taken at once from both layers indicated that the lower layer consisted of sulfamide containing benzoic acid, whereas the upper layer was benzoic acid with a few percent of sulfamide.

When heated to 125°, crystals soon made their appearance in the lower layer, and within two hours all of the lower layer solidified. Upon cooling the upper layer also crystallized. Treatment with ether dissolved all of the upper layer, the lower layer remaining undissolved. When acted upon by water, on the other hand, the lower layer dissolves readily, while the upper layer remains in the deposit. The most convenient way of separating the reaction products is to treat the reaction mixture with 10.0-15.0 ml of water and 50.0-75.0 ml of ether. The benzoic acid is extracted from the ether solution with 10 ml of 1 N sodium hydroxide; after the ether has been driven off, the benzamide (0.14-0.60 g) with a m.p. of 124-126° remains behind, its m.p. being 126-127° (uncorr.) after recrystallization from a small quantity of water. It exhibits no depression when mixed with a known sample of benzamide. 0.95 g of benzoic acid was recovered from the alkaline extract.

The aqueous solution was found to contain a small quantity of ammonium salts, a small quantity of sulfamic acid and sulfamide, and a considerable amount of products of the thermal decomposition of sulfamide. The next experiments were run at temperatures of 135-220°, for 30, 60, and 120 minutes, the sulfamide being taken in twice or three times the required amount for some of the tests.

In the best case (200% excess of sulfamide), we got 50% of the theoretical yield of benzamide and 40% of benzoic acid. At higher temperatures noticeable tarring occurred, the yields of benzamide dropped, and up to 50% of benzonitrile could be recovered from the reaction mixture. This latter aspect will be discussed in detail in subsequent reports.

Experiments on the Amidation of Benzoic Acid With Sulfamide in the Presence of Pyridine

At first, the reaction was carried out with equimolecular quantities of sulfamide and benzoic acid in the presence of 6-10 moles of pyridine per mole of the reagents; we were unable to obtain a benzamide yield that was higher than 50% of the theoretical quantity. We succeeded in ascertaining the reasons for this later on. It was found that sulfamide readily reacts with itself in the presence of pyridine at temperatures as low as 100°. In all probability,

the reaction product is the ammonium salt of imidosulfodiamide, or the diammonium salt of the trisulfamide. Moreover, the sulfamic acid formed during the reaction in the presence of pyridine readily interacts with the sulfamide, forming ammonium imidosulfonamate. This is why, in the case of benzoic acid, one and a half to two molecules of sulfamide must be used in the reaction for every molecule of the carboxylic acid. The reaction is very rapid at 125°, but the highest yields are obtained at a lower temperature with prolonged heating. Numerous experiments resulted in our discovering the optimum amidation conditions, as described below.

0.01 mole of benzoic acid (1.22 g) was mixed in a 50-100 ml round-bottomed flask with 0.02 mole of sulfamide (1.92 g) and 5 ml of pyridine (about 0.065 mole). All the reagents must be well desiccated ahead of time. The flask was sealed with a stopper fitted with an air-cooled reflux condenser and was then immersed in a boiling water bath. Dissolution was complete after a few seconds. After an hour had elapsed, a few crystals made their appearance in the transparent, colorless liquid; the crystals gradually grew, and by the time two and a half hours had passed, they almost filled all the liquid. No ammonia is evolved during the reaction, provided all the reagents used are anhydrous. After three hours had passed, the flask was lifted out of the bath, and most of the pyridine was driven off in vacuum. 10 ml of water or 10 ml of a 2.0 N solution of soda was added to the dry residue, and the mixture was again vacuum-evaporated to remove the pyridine more completely. 10 ml of water was again added to the dry residue, and the mixture rapidly heated to the boiling point. Much of the benzamide remained in the precipitate; it was chilled and left to stand in a cool place for three hours, after which the benzamide was drawn off and washed four times, using 5 ml of water each time. Drying yielded 0.9 g of benzamide, i.e., 74.4% of the theoretical quantity, with a m.p. of 125-127°; the m.p. was 126-127° (uncorr.) after recrystallization from a small quantity of water. It exhibited no depression of the melting point when mixed with a known test sample of benzamide.

The mother liquor was acidulated with 2 ml of 10.0 N sulfuric acid and then extracted four times, using 25 ml of ether each time. The combined ether extracts were washed with 2 ml of 1.0 N sodium hydroxide, filtered, and dried with sodium sulfate. The residue left after the ether had been driven off was recrystallized from 2 ml of water. This yielded 0.12 g of benzamide, i.e., another 9.9% of the theoretical quantity, with a m.p. of 126-127° (uncorr).

Thus, the overall yield of benzamide was 84.3% of the theoretical quantity.

0.03 g of benzoic acid was recovered from the alkaline extract after acidulation and extraction with ether.

Amidation of p-Nitrobenzoic Acid

A mixture of 0.01 mole of p-nitrobenzoic acid (1.67 g), 0.02 mole of sulfamide (1.92 g), and 5 ml of anhydrous pyridine was heated for three hours over a boiling water bath. All the reagents entered solution at once, after which crystals slowly began to separate out.

The pyridine was driven off in vacuum, 10 ml of water was added to the dry residue, the latter was again evaporated in vacuum, and 10 ml of water was again added to the dry residue, which was heated to boiling, chilled, drawn off, and washed. This yielded 1.55 g, i.e., 93.5% of the theoretical quantity, of p-nitrobenzamide, with a m.p. of 195-196.5°; recrystallization from water yielded nearly colorless needles a few centimeters long, with a m.p. of 196-197° (uncorr). They exhibited no depression when mixed with known p-nitrobenzamide; their properties agreed with those described in the literature [5]

Amidation of m-Nitrobenzoic Acid

The reaction was carried out under the same conditions as above, but only 0.015 mole of sulfamide was used per 0.01 mole of the acid. The yield of m-nitrobenzamide was 1.4 g, i.e., about 84% of theory. Recrystallization from water yielded hard prisms with a m.p. of 139-140° (uncorr.); they exhibited no depression when mixed with known m-nitrobenzamide; their properties agreed with those described in the literature, [8].

Amidation of o-Chlorobenzoic Acid

This was effected exactly as in the case of m-nitrobenzoic acid. 0.01 mole of o-chlorobenzoic acid (1.57 g) yielded 1.40 g of o-chlorobenzamide, i.e., 90% of the theoretical quantity. M.p. 140-141° (uncorr.); it exhibited no depression when mixed with known o-chlorobenzamide and its properties agreed with those described in the literature, [7].

Amidation of p-Chlorobenzoic Acid

This was effected under the same conditions as above, but only 0.0125 mole of sulfamide was used per 0.01 mole of the acid. The yield of the crude amide, with a m.p. of 165-167°, was 1.5 g, i.e., 96% of theory; needles with a m.p. of 169-171° (uncorr.) after recrystallization from water. It exhibited no depression when mixed with known p-chlorobenzamide, and its properties corresponded to those described in the literature [8].

Amidation of Acetic Acid

A mixture of 0.02 mole of glacial acetic acid (1.2 g), 0.03 mole of sulfamide (2.88 g), and 5 ml of anhydrous pyridine was heated for 3 hours over a boiling water bath. After cooling, 15 ml of a 2.0 N solution of soda was added to the reaction mixture, causing carbon dioxide to be liberated. The water and pyridine were driven off in vacuum at 40°, and the acetamide was extracted from the dry residue with acetone (four times, using 5 ml each time). After the acetone had been evaporated, the oily residue was dried in an exsiccator over sulfuric acid; within 24 hours it crystallized completely into long needles with a m.p. of 73-78°. The yield was 1.0 g, or 84% of theory; the m.p. was 80° (uncorr.) after recrystallization from water. It exhibited no depression when mixed with known acetamide, and its properties agreed with those described in the literature [8].

Amidation of Caprylic Acid

This amidation and the isolation of the caprylamide were effected exactly as in the case of p-chlorobenzoic acid, with 7.5 ml of a 2.0 N soda solution being added to the reaction mixture instead of water. The yield of caprylamide was 1.15 g (from 0.01 mole of acid), or 80% of theory; recrystallization from water yielded colorless, lustrous, fine lamellae, with a m.p. of 102-104° (uncorr.). It exhibited no depression when mixed with known caprylamide, and its properties agreed with those described in the literature [10].

Amidation of Palmitic Acid

A better yield is obtained if the reaction is carried out rapidly over an oil bath. A mixture of 0.005 mole of palmitic acid (1.28 g), 0.01 mole of sulfamide (0.96 g), and 2 ml of anhydrous pyridine was heated for 30 minutes with an air-cooled reflux condenser over an oil bath heated to 130°.

The pyridine was then driven off in vacuum, 10 ml of water was added, the whole heated to boiling, again evaporated in vacuum, 10 more ml of water was added, again heated to boiling, 10 ml of 1.0 N potassium hydroxide was added,

and the mixture boiled for 1 minute, cooled with shaking, drawn off, and washed with a 0.5 N soda solution (without squeezing). The precipitate was dried in air and extracted with boiling acetone (three times, using 50 ml each time); the acetone extracts were evaporated to a volume of 40 ml and then left to crystallize. A few hours later they were drawn off and washed with acetone. This yielded 0.8 g of palmitamide as snow-white finely crystalline powder. The mother liquor was evaporated to a volume of 5 ml, which yielded another 0.23 g of the amide.

The aggregate yield was 1.03 g, or 81.5% of theory; m.p. 102-103° (uncorr.). It exhibited no depression when mixed with known palmitamide, and its properties agreed with those described in the literature [11].

Amidation of Phenylacetic Acid

This amidation and the isolation of the phenylacetamide were effected as in the case of caprylic acid. 0.01 mole of the acid yielded 0.04 g of the amide, i.e., 70% of theory. Recrystallization from water yielded lustrous lamellar platelets with a m.p. of 154-155° (uncorr.); they exhibited no depression when mixed with known phenylacetamide, and their properties agreed with those described in the literature [12].

SUMMARY

A new method has been developed for the synthesis of amides of carboxylic acids directly from the acids themselves by the action on these acids of sulfamide in the presence of pyridine.

This new method has been tested on a number of monobasic carboxylic acids of the acyclic and aromatic series.

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BETAINE-LIKE COMPOUNDS FORMED WHEN A PROTON IS SPLIT OFF FROM AN NH GROUP. III

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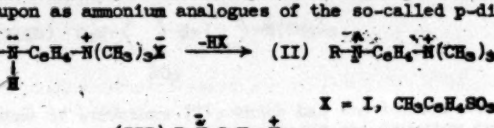
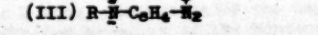
It has been shown in previous reports [1] that when alkaline agents act upon quaternary ammonium salts of the diphenylamine series (I. R = 2,4-dinitrophenyl, picryl), characteristic inner quaternary salts of structure (II), which we call betaine-azeniates,* are readily formed. The para isomers of this series may be looked upon as ammonium analogues of the so-called p-diazoimines (III) [2]:

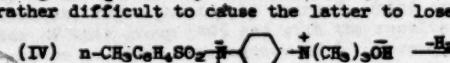


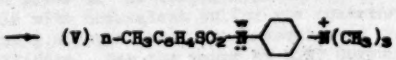
X = I, $CH_3C_6H_4SO_3$



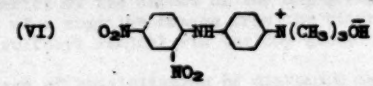
A necessary condition for the formation of bipolar ions of this type is the adequate mobility of the proton in the NH group; for a number of synthesized compounds, it is dependent upon the influence of the ammonium group, which is exerted via the inductive effect, and of the dinitrophenyl (or picryl) group. We might therefore expect that quaternary salts that contain an aryl sulfonyl group (I, R = $ArSO_2$), which possesses a stropg inductive effect, instead of the dinitrophenyl radical, could be easily transformed into betaine-azeniates. The p-diazoimines (III, R = $ArSO_2$), which have a similar structure, are readily formed, as we know, by the action of weakly alkaline agents upon aqueous solutions of the corresponding diazonium salts [3].

Our experiments have shown, however, that under these conditions the iodomethylate of 4-(p-toluenesulfamino)-dimethylaniline, as well as its meta isomer, does not form a betaine. The synthesis of methylbetaine (V) is effected only by dehydrating the quaternary ammonium base (IV) obtained from the iodomethylate, it being rather difficult to cause the latter to lose water:





Thus, the tendency for a proton to be split off from the NH group, forming betaine as a result, is less pronounced in the initial quaternary compound than in the derivatives of diphenylamine that we investigated previously [1]. In fact, a quaternary base of structure (VI) is partially converted into betaine even in dilute aqueous solution as is shown in the experimental section below.



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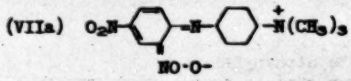
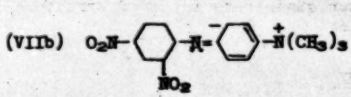
*By analogy with the terms: phenolbetaines, acinitrobetaines, etc., we might also have used the term iminobetaines for the compounds we investigated.

To provide an explanation of these phenomena, it must be assumed that within the betaine-azeniate molecule the system of the bivalent negatively charged (azeniatic) N atom is stabilized by mesomeric shifts. In the presence of strongly electrophilic groups linked to the N atom, which cause a reduction of the negative charge on the N atom as the result of a mesomeric shift of electrons to these groups, a bipolar ion may be formed readily. Such structural singularities are present in the betaine molecules of the diphenylamine series, where the mesomeric effect of two phenyl groups directly linked to the N atom is manifested (cf, for example, Formulas VIIa and VIIb).*

(VIIa) 

(VIIb) 

In the betaine of structure (V), which has the toluene sulfonyl radical attached to the azeniatic N atom, diminution of the negative charge on the N atom by mesomeric shifts is effected by means of the benzene ring linked to the ammonium group and the SO_2 group. As a result of contrary electron displacements the benzene ring of the toluenesulfonyl group exerts an influence that is opposed to that of the SO_2 group; this may be expressed, for instance, by means of Diagram (VIII):

(VIII)

As a result, the toluenesulfonyl group proves to be heterodynamic in its effect upon the N atom of the dinitrophenylgroup, and its tendency to form a bipolar ion (V) is weakened.

The problem of the electronic structure of the RSO_2 group has not been finally settled as yet. In this group the sulfur may be conceived of as quadrivalent, twice positively charged, which agrees with the chemical behavior of this group [10] and with the results of parachore measurements, or it may be assigned a covalency of 6. Several weighty arguments, based on a study of the dipole moments and the length of the S-O bonds [11], are advanced in favor of the latter hypothesis. Interesting data in support of a formula with hexavalent sulfur are contained in a paper by K.M. Khaikina and I.M.Kogan [12], who investigated the properties of the copper salt of sulfidine. See the paper by E.N. Guryanova [9] for the effect of the NH_2SO_2 group upon the ring.

If we assume that the sulfur in the aryl sulfonyl group is hexavalent, the $-SO_2-$ group must be assigned a strong mesomeric effect in addition to its inductive effect. No matter what the mechanism (inductive or mesomeric) of the effect of the SO_2 group upon the azeniatic N atom, the shift of a negative charge from the nitrogen to the benzene ring of the aryl sulfonyl radical via the SO_2 group is impossible.

The ease of betainization of diazonium salts that contain an aryl sulfonyl radical (III, R = $ArSO_2$) attached to the NH group, which are characterized by the

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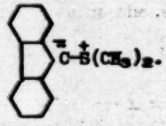
* See the paper by V. A. Izmailsky and Simonov [7] for a discussion of the mesomeric shifts within the diphenylamine molecule.

readiness with which they are transformed into a betaine (diazoimine), as indicated above, is due to the influence of the extremely strongly electrophilic diazonium group. In fact, if the influence of the $C_6H_4N_2$ group upon the NH group is cut out by introducing a barrier in the shape of a CH_2 group, no diazoimine is formed [4].

The stabilizing effect of strongly electrophilic groups may be traced in a few internal sulfonium salts of the fluorene series [5,6]. The compound with structure (IX) is not very stable [6]. Stability is increased by increasing the electrophilic nature of the system by introducing a nitro group at position 2 [6]; the stability of a bipolar ion is raised still higher by introducing another nitro group (at position 7).

The introduction of a nitro group has a similar effect upon the stability of 4-diazodiphenylamine [2]:

(IX)  $C-\overset{+}{S}(CH_3)_2$.

EXPERIMENTAL

4-(p-Toluenesulfamino)-N,N-dimethylaniline

This compound is synthesized by heating p-toluenesulfochloride with vacuum-distilled p-aminodimethylaniline (4% excess) in an alcoholic solution in the presence of sodium acetate. The precipitate, which contains traces of the amine acetate, is dissolved in dilute hydrochloric acid, the base being isolated by sodium bicarbonate (70% yield) and then repeatedly recrystallized from benzene and alcohol. The colorless crystals, with a m.p. of 131-132°, are readily soluble in caustic alkali.

A substance with the same properties is produced by effecting the acylation in a solution of pyridine bases (b.p. 115-135°). Yield = about 90%.

0.2480 g substance: 0.1976 g $BaSO_4$ (Carius).
0.2240 g substance: 0.1785 g $BaSO_4$
Found %: S 10.94, 10.92.
$C_{15}H_{18}O_2N_2S$. Calculated %: S 11.04.

Iodomethylate of 4-(toluenesulfamino)-N,N-dimethylaniline

4.3 g of 4-(p-toluenesulfamino)-dimethylaniline and 2.2 g (10% excess) of methyl iodide were heated to boiling in a solution of anhydrous benzene. The yield after 2 hours of heating was 4.9 g (81%) Lustrous needles (from 90% alcohol or water) with an unsharp temperature of decomposition, lying between 187 and 193°, depending upon the rate of heating.

0.2228 g substance: 0.1143 g AgI.
0.1301 g substance: 0.0706 g AgI.
Found %: I 29.25, 29.33.
$C_{16}H_{21}O_2N_2SI$. Calculated %: I 29.36.

Methyl-p-toluenesulfonate of 4-(p-toluenesulfamino)N,N-dimethylaniline

A mixture of 1.45 g of 4-(p-toluenesulfamino)-dimethylaniline and 0.90 g of methyl p-toluenesulfonate were heated for 1 hour over an oil bath at a temperature of 120°. Upon cooling the melt was pulverized and washed with hot benzene. The residue (2.1 g) was purified by dissolving it in a small amount of alcohol and precipitating it from the solution with ether. Triple precipitation yielded 1.5 g of grayish white crystals with a m.p. of 220°.

0.2002 g substance: 0.1951 g $BaSO_4$ (Carius)
0.2199 g substance: 0.2141 g $BaSO_4$.
Found %: S 13.38, 13.37.
$C_{23}H_{28}O_5N_2S_2$. Calculated %: S 13.45.

3-(p-Toluenesulfamino)-N,N-dimethylaniline

The compound was prepared by heating m-aminodimethylaniline and p-toluenesulfochloride in an alcoholic solution in the presence of sodium acetate. This yielded a white crystalline product (from a mixture of benzene and petroleum ether) with a m.p. of 150.5-151°.

0.2036 g substance: 0.1622 g $BaSO_4$ (Carius).
0.1552 g substance: 0.1238 g $BaSO_4$.
Found %: S 10.94, 10.96.
$C_{15}H_{18}O_2N_2S$. Calculated %: S 11.04.

Iodomethylate of 3-(p-Toluenesulfamino)-N,N-dimethylaniline

Colorless crystals (from alcohol), with a m.p. of 172-175°.
0.2126 g substance: 0.1146 g AgI.
Found %: I 29.14.
$C_{16}H_{21}O_2N_2SI$. Calculated %: I 29.36.

Methylbetaine of 4-(p-Toluenesulfamino)-N,N-dimethylaniline (V)

When moist silver oxide is reacted with an aqueous solution of the iodomethylate of 4-(p-toluenesulfamino)-dimethylaniline, part of the silver remains in the solution in the combined state and contaminates the quaternary base obtained by evaporating the solution. For this reason, the iodomethylate (2.0 g) was first converted into a sulfate by the action of an equivalent quantity of silver sulfate, the solution was evaporated to dryness in vacuum, and the quaternary salt was purified by precipitating it by ether from an alcoholic solution. The sulfate obtained (1.50 g) was further transformed into a base; this was done by dissolving it in 35 ml of water and duly precipitating the sulfate ion from the hot solution with a 0.4 N solution of barium hydroxide; the filtrate was then evaporated to dryness in vacuum (30 mm), and the residue was dried in an exsiccator over sodium hydroxide. The product, which still contained more than half a molecule of water per molecule of betaine, was further dehydrated by heating it for several hours to 80°* in vacuum (20 mm) or by allowing it to stand for a long time (several days) in a vacuum exsiccator over phosphorus pentoxide. The betaine yield was 0.98 g.

The compound was purified by dissolving it in hot absolute alcohol (50 ml) and precipitating it from solution with absolute ether.** This yielded white acicular crystals with an unsharp decomposition temperature (above 220°), depending on the initial temperature and the rate of heating. The compound, which

* Heating in vacuum to above 100 ° caus s the quaternary base to begin to decompose, forming a tertiary amine.

** The conversion to betaine takes place before dissolution in absolute alcohol; this is proved by analysis of the product before reprecipitation.

is insoluble in chloroform or benzene, is readily soluble in water, forming a colorless solution that yields an alkaline reaction with litmus paper.

0.1199 g substance (before reprecipitation): 9.85 ml N_2 (23.5°, 753 mm).
0.1095 g substance (after reprecipitation): 9.20 ml N_2 (21.5°, 748 mm).
0.1325 g substance: 0.1002 g $BaSO_4$ (Carius).
0.1438 g substance: 0.1093 g $BaSO_4$.
Found %: N 9.17, 9.39; S 10.39, 10.44.
$C_{18}H_{20}O_2N_2S$. Calculated %: N 9.20; S 10.53.

Reaction of the Iodomethylate of 4-Dimethylamino-2',4'-dinitrodiphenylamine With Moist Silver Oxide

0.44 g of the iodomethylate was dissolved in 150 ml of water at 50°, and silver oxide, prepared from 1 g of silver nitrate and carefully washed with hot water, was added in small batches to the bright yellow solution. Shaking the solution causes it to turn reddish orange, owing to the formation of an equilibrium mixture of the yellow quaternary base and the dark-red betaine. The precipitate of silver iodide is filtered out, and the filtrate is evaporated in vacuum (30-35 mm).

As the water is driven off, the color of the solution turns darker, finally acquiring a dark red color. When the volume of the liquid was reduced to 10 ml, a crystalline blackish-red precipitate of betaine begins to settle out. It is dried in an exsiccator over alkali. The yield of methylbetaine of 4-dimethylamino-2',4'-dinitrodiphenylamine was 0.28 g (about 90%).

SUMMARY

1. The synthesis of a betaine-azeniate of structure (V) with a toluenesulfonyl group attached to the azeniatic N atom, formed in the dehydration of the base (IV) is described. Formation of this compound is more difficult than that of the betaine-azeniates of the diphenylamine series previously described.

2. Explanation of this phenomenon requires the assumption that in the betaine-azeniate molecule (V) there is a lesser possibility of stabilization via a mesomeric shift of electrons from the bivalent, negatively charged N atom (originating in the splitting off of a proton from the NH group) toward the electrophilic groups linked to it.

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June 27, 1948

THE PRESENCE OF HYDRINDAN IN SURAKHANY GASOLINE

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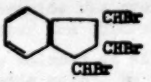
Fuel Institute of the USSR Academy of Sciences

Notwithstanding the extensive and successful research that has been done on the constituent hydrocarbons of petroleum, there still remains a class of hydrocarbons that has not been touched in all this research. The class we have in mind is hydrindan.

The presence of a naphthene with two condensed six-membered rings (decalin) in petroleums justifies our raising the question of the presence of a hydrocarbon with two condensed rings, one of them six-membered and the other five-membered (hydrindan). We did considerable preparatory work [1] in connection with this planned investigation, involving the synthesis of several derivatives of pure hydrindan and a study of their properties. This work was based upon the nitration method developed by Konovalov. The research yielded many interesting observations [1] and at the same time demonstrated the impossibility of applying this method to the narrow fractions of Surakhany gasoline, owing to the instability of these nitro compounds (their rapid tarring). The method could be used only when large amounts of hydrindan were present, which was out of the question in the narrow gasoline fractions. We therefore chose a different approach, based upon the fact that the bromination of hydrindene in a chloroform solution yields tribromohydrindene upon boiling [2]:

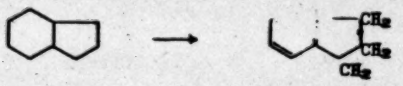


which readily converts into phthalic acid when oxidized with potassium permanganate.

With this as a basis, we first worked out a method for determining the percentage of hydrindene in artificial mixtures. These artificial mixtures were prepared from dearomatized Grozny gasoline and hydrindene. Mixtures containing 3, 5 and 10% of hydrindene were subjected to bromination [2]. Tribromohydrindene crystallized out of the mixture containing 10% of hydrindene within a day, whereas it took 2 weeks to crystallize out of the 5% mixture, and a year and a half to crystallize out of the 3% mixture. We then proceeded to our investigation of Surakhany gasoline to determine whether it contained hydrindan.

The Surakhany gasoline was distilled into narrow fractions. The fraction with a boiling point of 160-167° was dearomatized by treating it with 100% sulfuric acid, after which it was refractionated. The fraction with a b.p. of 161.5-165° (close to the boiling point of hydrindan) and a n_D^{15} 1.4322 was dehydrogenated over a Pt catalyst on charcoal to a n_D^{15} 1.4470.

Thus, if any hydrindan (I) was present in the given fraction, it would have been converted into hydrindene (II).



(I) (II)

The dehydrogenated fraction, like the artificial mixtures, was brominated [2] and then recrystallized from a mixture of alcohol and glacial acetic acid. Two weeks later a very small quantity of uncharacteristic tiny crystals appeared. Oxidation by potassium permanganate in an alkaline medium yielded a small amount of a substance that changed into fluorescein when fused with resorcinol; this is characteristic of phthalic acid alone. Finally, when phthalic acid is oxidized with potassium permanganate, it may yield other bromides, in addition to tribromohydrindene.

We examined the constants of all hydrocarbons that might be the source of this phthalic acid without finding a single one whose boiling point fell within the 161.5-165° fraction. This fact convinces us that there are hydrindan hydrocarbons in Surakhany petroleum, though they constitute no more than 3% of the fraction.

EXPERIMENTAL

1. Bromination of Hydrindene

4.5 g of hydrindene was dissolved in twice its weight of chloroform, and a solution of 21 g of bromine in chloroform was gradually added while the first solution was boiled with a reflux condenser (ground-glass connection). Large quantities of hydrogen bromide were liberated, flowing off through the outlet tube. After all the bromine had been added, the solution was boiled for another 6 hours, until no more hydrogen bromide was evolved. The tribromohydrindene left in the flask crystallized after the chloroform had been driven off.

Tribromohydrindene is hardly soluble at all in ethyl alcohol, whereas it is readily soluble in glacial acetic acid; We therefore purified it by recrystallizing it from a mixture of ethyl alcohol and glacial acetic acid. It separated out as large, flat, feathery crystals with a m.p. of 134-135°, which were intensely lachrymatory.

2. Oxidation of Tribromohydrindene

Finely ground tribromohydrindene was heated in an alkaline solution of potassium permanganate until the color changed. Then the deposit of manganese dioxide was filtered out, and the residual permanganate decomposed with alcohol, the precipitated manganese dioxide being filtered out again. The alkaline solution was evaporated and then acidulated with hydrochloric acid. Upon standing, phthalic acid crystallized out in a mixture with sodium chloride. Heating this mixture caused phthalic anhydride, with a m.p. of 129-130°, to sublimate.

It should be noted that some solvent, such as ether, benzene, and the like, must be added during the oxidation of tribromohydrindene, as otherwise the tribromohydrindene would escape with the steam and condense in the condenser.

3. Research on Artificial Mixtures

The fraction of dearomatized Grozny gasoline with a b.p. of 150-170° was used to prepare the artificial mixtures.

Mixture 1: 9 g of gasoline, 1 g of hydrindene, i.e., 10% of hydrindene.

Mixture 2: 9.5 g of gasoline, 0.5 g of hydrindene, i.e., 5% of hydrindene.

Mixture 3: 9.7 g of gasoline, 0.3 g of hydrindene, i.e., 3% of hydrindene.

All these three mixtures were brominated and then treatedas described above for hydrindene. Mixture 1 required 20 g of bromine, Mixture 2 - 10 g, and Mixture 3 - 6 g of bromine. After bromination was complete, the chloroform was driven off, and all the liquid product was then distilled at atmospheric pressure and in vacuum. The solid residue (bromides) were boiled for some time with glacial acetic acid. The insoluble portion was filtered out, and 75% of the acetic acid distilled off. The mixture, diluted with twice its weight of alcohol, was then boiled for a long time, after which the tar that settled was again filtered out, half the solvent was driven off, and the rest was left to crystallize.

Crystals of tribromohydrindene separated out the next day from Mixture 1, two weeks later from Mixture 2, and a year and a half later from Mixture 3.

4. Fractionation of Surakhany Gasoline

We began by fractionating 120 liters of Surakhany gasoline in a 200-liter semi-industrial still and a 3-meter tower, collecting 10° fractions. Then the 150-160° and 160-170° fractions were repeatedly distilled in the laboratory into a 60 cm tower (designed by G.D.Halpern*), and separated into the following fractions: 150-155°, 155-160°, 160-167°, and 167-175°.

5. Dearomatizing the 160-167° Fraction

We twice treated the 160-167° fraction with twice its volume of 100% sulfuric acid.

The first treatment yielded the following results: before treatment – n_D^{15} 1.4425; after 30 minutes – n_D^{15} 1.4345; after 1 hour n_D^{15} 1.4322.

The spent acid was replaced by a fresh batch. After agitation for 30 minutes, n_D^{15} 1.4322; after agitation for 1 hour, n_D^{15} 1.4322.

The dearomatized products were again fractionated after being neutralized, washed, and dried. This yielded 21 g of a product with a b.p. of 161.5-165°, and a n_D^{15} 1.4322.

6. Dehydrogenating the Dearomatized Fraction

We dehydrogenated the 161.5-165° fraction with a Pt catalyst on charcoal at a temperature of 300-310° and at a rate of 1 to 2 drops per minute. Dehydrogenation was effected in a current of carbon dioxide.

The refractive index changed as follows:

1st pass:	n_D^{15} 1.4390;
2nd pass;	n_D^{15} 1.4430;
3rd pass:	n_D^{15} 1.4470;
4th pass:	n_D^{15} 1.4470.

7. Bromination and Oxidation of the Dehydrogenated Fraction of Surakhany Gasoline

13 g of dehydrogenated Surakhany gasoline was dissolved in 20 ml of chloroform, and a solution of 10 g of bromine in chloroform was gradually added to the

* Izv. USSR Acad. Sci. 1937, p. 958.

boiling solution, causing large quantities of hydrogen bromide to evolve.

When the reaction was over, the chloroform was driven off. The residue was a very viscous substance that could not be distilled in vacuum. We treated it with glacial acetic acid, from which we succeeded in recovering tribromohydrindene. After 75% of the acetic acid had been driven off, and the solution been diluted with twice its weight of ethyl alcohol, we succeeded in recovering a small quantity of a crystalline substance, which was at once oxidized with potassium permanganate. After acidulation with hydrochloric acid, the oxidation products were extracted with sulfuric ether. After the ether had been driven off, there remained in the flask a minute quantity of a solid substance with a m.p. of about 198° (the melting point of phthalic acid is 200°). The small amount of product recovered made it impossible to recrystallize it. The substance sublimed when heated, yielding a product with a m.p. of 122°, which is close to the melting point of phthalic anhydride. The product was converted into fluorescein when it was fused with resorcinol.

This proves that the product of the oxidation of the bromides was phthalic acid.

SUMMARY

It has been shown that the hydrindan in Surakhany gasoline is no more than 3% of the 161.5-165° fraction, or approximately 0.003% in terms of the whole gasoline.

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XXV. CATALYTIC DEHYDRATION OF 1,4-AMINOHYDROXYBUTANE

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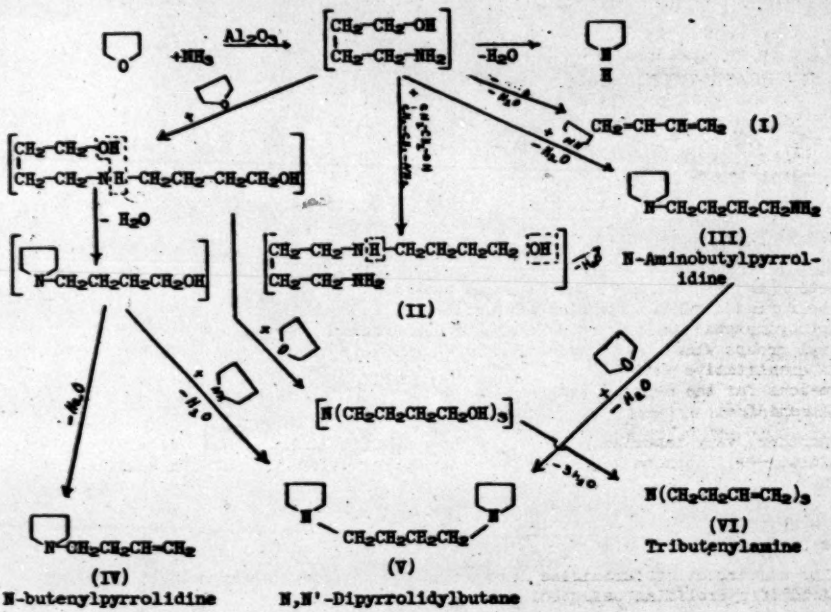
In one of our previous reports, devoted to a study of the mechanism of the catalytic conversion of heterocyclic compounds containing oxygen into rings with other hetero atoms, we demonstrated that the intermediate substance that must be formed in the conversion of furanidine into thiophane, namely, 1,4-mercaptohydroxybutane, undergoes complete dehydration of the sulfhydryl and hydroxyl groups when passed over alumina at 400°, [1], resulting in thiophane with a quantitative yield (95% of the theoretical). This is, no doubt, one of the reasons for the nearly quantitative yield of thiophane when it is synthesized from furanidine.

Another, very important factor responsible for the smoothness of the furanidine ⟶ thiophane reaction is the specific action of hydrogen sulfide on the furanidine ring in the presence of alumina at high temperatures: this agent, which is of an acid character, acts upon the carbon-oxygen bond of the ring, which must result in the exhaustive formation of 1,4-mercaptohydroxybutane [2] in the intermediate phase.

The conversion of furanidine into pyrrolidine proceeds somewhat differently, the yield of pyrrolidine being 46.5% of the theoretical.

The reasons for the smaller yield of pyrrolidine (compared to the yield of thiophane) should be the absence of so marked an action of ammonia upon a given point of the furanidine molecule and the low stability of the intermediate product, 1,4-aminohydroxybutane. The low stability of the latter may, for instance, manifest itself in the breaking off of the amino group in the form of ammonia (which we have observed). This side reaction may, however, be considerably retarded by reducing the time of contact and by carrying out the conversion of furanidine with a very large excess of ammonia.

The 1,4-aminohydroxybutane formed in the intermediate stage of the conversion reaction can react via its amino group with furanidine and with the hydroxy group of another hydroxyamine molecule, and via its hydroxy group with the imino group of the pyrrolidine, which ought to lead to the formation of the following by-products of the reaction:



The present paper treats of the behavior of 1,4-aminohydroxybutane in the presence of aluminum oxides at 350 and 400° when no ammonia is present, and when it is present; in not a single experiment did the yield of pyrrolidine even approach the yields obtained in the conversion of furanidine into pyrrolidine, falling far below them.

Table 1

Temperature, °	Initial substance	Amount of initial substance, g	Constants of the synthesized pyrrolidine			Yield of pyrrolidine	
			b.p., °	d_4^{20}	n_D^{20}	in g	% of theory
300	Furanidine + NH_3 [3]	5.0	–	–	–	–	Negligible
350	Furanidine + NH_3 [3]	4.9	85.5-88	–	1.4421	1.5	30.5
	1-Amino-4-hydroxybutane	6.0	85-87	–	1.4429	1.2	25.0
	1-Amino-4-hydroxybutane + NH_3	5.0	85-86.5	–	1.4430	0.78	20.0
400	Furanidine + NH_3 [4]	10.0	85.4-86.4	0.8576	1.4428	4.6	46.5
	1-Amino-4-hydroxybutane	7.0	85-87	0.8599	1.4431	2.0	37.0
	1-Amino-4-hydroxybutane + NH_3	5.0	85-86	0.8606	1.4425	0.93	29.0

The lower yields of pyrrolidine in the catalytic dehydration of 1,4-aminohydroxybutane are doubtless due to the fact that in this reaction the following were predominant among the possible side reactions: the splitting off of water and ammonia (I); the intermolecular condensation of the hydroxyamine molecules (II and III); and reaction with the pyrrolidine (III) formed.

Comparative data on the synthesis of pyrrolidine by the catalytic dehydration of 1-amino-4-hydroxybutane and the catalytic conversion of furanidine are listed in Table 1.

EXPERIMENTAL

1,4-Aminohydroxybutane was synthesized by means of the following series of reactions:

$$ClCH_2CH_2CH_2Br \xrightarrow[H_2O]{K_2CO_3} HOCH_2CH_2CH_2OH \xrightarrow{HCl} ClCH_2CH_2CH_2OH \xrightarrow{KCN}$$

$$\longrightarrow NCCH_2CH_2CH_2OH \xrightarrow[(Na + alcohol)]{H_2} H_2NCH_2CH_2CH_2CH_2OH$$

a) Trimethyleneglycol was synthesized by the method [5] used for synthesizing glycols from dihalides by boiling the latter in a potash solution. Trimethyleneglycol possessed the following constants:

B.p. 108-110° (10 mm); d_4^{20} 1.0497; n_D^{20} 1.4398; MR_D 19.09.

$C_3H_8O_2$. Calculated MR_D 19.10.

The yield was 89% of the theoretical.

Literature data on trimethyleneglycol: B. Fortinsky [6]: B.p. 214-216° (760 mm); d_4^{18} 1.0526.

b) Trimethylenechlorohydrin was synthesized by the method described in Syntheses of Organic Preparations' [7]:

B.p. 60-64° (10 mm); d_4^{20} 1.1322; n_D^{20} 1.4485; MR_D 22.37.

C_3H_7OCl. Calculated MR_D 22.44.

Literature data on trimethylenechlorohydrin: B.p. 160-160.3° (760 mm); d_4^0 1.1490; d_4^{20} 1.1309 [8].

c) Trimethylenehydroxynitrile was synthesized by the method used for the synthesis of ethylenehydroxynitrile [8].

110 g of trimethylenechlorohydrin and 510 ml of ethyl alcohol were placed in a 1000-ml round-bottomed flask fitted with a reflux condenser, a stirrer with a mercury seal, and a dropping funnel. The alcoholic solution was heated to boiling (over a water bath), and then a solution of 96 g of potassium cyanide in 145 ml of water was added drop by drop, with vigorous stirring. A precipitate of potassium chloride began to settle at once, and the reaction mass turned yellow. Heating was continued for another 8 hours (with stirring) to complete the reaction, after which the reaction mixture was set aside to stand overnight. The precipitate was filtered out of the dark-red solution and washed several times with alcohol; the combined water-alcohol solutions of the hydroxynitrile were then reduced (by driving off the water and alcohol from the flask with a dephlegmator) until they had the consistency of a syrup (a volume of about 100 ml). The small precipitate that settled was filtered out and washed with alcohol, the wash alcohol being added to the bulk of the crude hydroxynitrile. After the alcohol had been driven off, the crude hydroxynitrile was fractionated at 30 mm, the following fractions being collected:

Fraction 1: up to 120°; Fraction 2: 120-130°. Fraction 3: 130-140°.

The third fraction was trimethylenehydroxynitrile. The yield was 55 g (56% of the theoretical).

Pure trimethylenehydroxynitrile has the following constants:

B.p. 135-136° (30 mm); d_4^{20} 1.1036; n_D^{20} 1.4478; MR_D 20.63.

C_4H_7ON. Calculated MR_D 22.015.

Literature data on trimethylenehydroxynitrile: b.p. 238-240° (765 mm); 130-140° (30 mm); d_4^{18} 1.1029 [10].

d) 1-Amino-4-hydroxybutane was prepared from the trimethylenehydroxynitrile by the method of synthesizing aliphatic amines [11]; the δ-aminobutanol was isolated by the method described by A.I. Kipriyanov and B.A.Roshkovan [12] for the preparation of δ-aminopropanol.

21 g (0.25 mole) of trimethylenehydroxynitrile and 200 ml of absolute n-butyl alcohol were placed in a 1000-ml round-bottomed flask fitted with a Y-adapter and a reflux condenser. The mixture was heated to boiling over a water bath, and 13 g of metallic sodium (in one piece) was added through the adapter After the extremely violent reaction (accompanied by the expulsion of some of the alcohol through the condenser) had quieted down, the reaction mixture was heated until all the sodium had dissolved. After the reaction mixture had cooled and 100 ml of water had been added, it was transferred to a 500-ml flask fitted with an outlet tube blown into its side. The alcohol, water, and amino alcohol were driven off to complete dryness. 30 to 40 ml of water was added to the dry residue in the flask, and the contents again evaporated to dryness; this was repeated 4 to 5 times until the distillate had a neutral reaction. The water and the butyl alcohol were driven off from the combined distillates, after the latter had been acidulated with hydrochloric acid, until approximately 100 to 120 ml of aqueous solution of the hydroxyamine hydrochloride was left (to remove all the alcohol the water was added a few times, and distillation was repeated until all the alcohol had been driven off). Then the solution was saturated with a concentrated solution of potassium hydroxide (until its reaction was strongly alkaline), and the water and amino alcohol were driven off until the flask's contents were completely dry; water was added to the dry residue in the flask several times, and the evaporation to dryness repeated until the distillate had a neutral reaction.

Water was expelled from the distillate, which contained an aqueous solution of the amino alcohol, very slowly (up to 110° with a high dephlegmator), and then the oily residue was transferred to a 15 ml flask fitted with a dephlegmator and fractionated twice. The 1-amino-4-hydroxybutane recovered (10 g yield, or 24% of the theoretical) possessed the following constants:

B.p. 207-208° (755 mm); d_4^{20} 0.9688; n_D^{20} 1.4581; MR_D 25.10.

$C_4H_{11}ON$. Calculated MR_D 25.62.

Literature data on 1-amino-4-hydroxybutane: b.p. 206° (760 mm); d_4^{20} 0.967 [13]; B.p. 100° (15 mm) [14].

Catalytic Dehydration of 1-Amino-4-hydroxybutane

Experiment 1. 400°. 7 g of 1-amino-4-hydroxybutane was passed over Al_2O_3 in a current of nitrogen at a rate of 5-6 drops per minute. The receiver was chilled with a mixture of dry ice and alcohol. After the usual treatment of the catalysis product and distillation of the reaction product (with a dephlegmator)

we recovered 2 g of pyrrolidine (37% of the theoretical yield).

B.p. 85-87° (758 mm); d_4^{20} 0.8599; n_D^{20} 1.4431; m.p. of the picrate 111.5°.

The residue in the flask exhibited the pyrrole reaction.

Experiment 2. 350°. 6 g of 1-amino-4-hydroxybutane, passed over Al_2O_3 in a current of nitrogen, yielded 1.2 g of pyrrolidine: b.p. 85-87°; n_D^{20} 1.4429. The yield was 25% of the theoretical. The residue in the flask exhibited the pyrrole reaction.

Experiment 3. 400°. 5 g of 1-amino-4-hydroxybutane was passed over Al_2O_3 in a current of ammonia at the rate of 6 drops per minute. This yielded 0.93 g of pyrrolidine. Yield: 29% of the theoretical; b.p. 85-86° (756 mm); n_D^{20} 1.4425; d_4^{20} 0.8606. A distillate (0.33 g) was recovered from the residue; it exhibited a pyrrole reaction, had a b.p. of 130-132°, n_D^{20} 1.5010, and was pyrrole.

Experiment 4. 350°. 5 g of 1-amino-4-hydroxybutane, passed over Al_2O_3 in a current of ammonia, yielded 0.78 g of pyrrolidine: b.p. 85-86.5° (756 mm); n_D^{20} 1.4430. Yield: 20% of the theoretical. The residue in the flask exhibited the pyrrole reaction.

In all these experiments the catalyst was covered with a dense black carbon deposit, indicating the marked decomposition of the 1-amino-4-hydroxybutane.

SUMMARY

It is shown in the present paper that 1-amino-4-hydroxybutane – an intermediate substance in the conversion of furanidine to pyrrolidine – undergoes dehydration in the presence of Al_2O_3, forming pyrrolidine. This reaction is complicated by the intensive decomposition of the amino alcohol. Dehydration in a current of nitrogen yields better results than dehydration in a current of ammonia.

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